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OF THE

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But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions;* which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them: without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

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By A. E. H. Tutton, *D.Sc., M.A., F.R.S., President of the Mineralogical Society.*

Received June 8,—Read June 17, 1915.

In this communication are described the five remaining double sulphates of the series $R_2M(SO_4)_2 . 6H_2O$, in which R is ammonium and M is nickel, cobalt, manganese, copper, and cadmium. The ammonium salts, in which M is magnesium, zinc, and iron, have been described in two previous communications,*† in the latter of which (that concerning ammonium ferrous sulphate) a number of general questions concerning the whole series were also discussed. The present contribution completes the author's work, commenced in the year 1890, on the double sulphates of this important monoclinic series, in all 31 salts, of which the R bases have been potassium rubidium, cæsium, ammonium, and thallium. Excluding thallium—of which only the zinc double sulphate has been included, the other double salts containing thallium not having yet been obtained in crystals of the perfection necessary for detailed accurate work of the character regarded as essential by the author—the four bases, potassium, rubidium, cæsium, and ammonium should give rise, with the eight several dyad bases above enumerated, to 32 double sulphates. All these have been obtained in excellent crystals, and fully described, with the two exceptions of potassium manganese and potassium cadmium sulphates, which, for some as yet undiscovered reason, are incapable of preparation. Yet so thoroughly are the relations between the various salts, and the rules governing the replacement of any one alkali base by any other, now understood, that it has been found possible to predict the constants of the two missing salts. Of the isomorphous double selenates, nine salts (including thallium zinc selenate) containing magnesium and zinc as M metals have already been described by the author, and it is intended that the remaining double selenates, those containing the other dyad metals, shall form the subject of the author's next communication.

---

* 'Journ. Chem. Soc., Trans.,' 1905, vol. 87, p. 1123.

† 'Roy. Soc. Proc.,' A, 1913, vol. 88, p. 361.

[Published October 30, 1915.

Ammonium Nickel Sulphate, $(NH_4)_2Ni(SO_4)_2 . 6H_2O$.

Morphology.

The first measurements of the crystals of this salt were made 60 years ago by MARIGNAC,* and the salt was included four years later by MURMANN and ROTTER† in their comprehensive crystallographic investigation. The forms observed in both investigations were the same as those given in the list below, except *a* {100} and *o* {111}, and the values observed for the principal angles will be found quoted in the two last columns of the table of angles.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—*a* : *b* : *c* = 0·7373 : 1 : 0·5000. Values of MURMANN and ROTTER, 0·7370 : 1 : 0·5032.

Axial Angle.—β = 106° 57′. Value of MURMANN and ROTTER, 107° 4′.

Forms Observed.—*a* {100}, *b* {010}, *c* {001}, *p* {110}, *p*′ {120}, *q* {011}, *r*′ {$\bar{2}$01}, *o* {111}, *o*′ {$\bar{1}$11}.

Habit.—Short prismatic parallel *p* {110}, or more or less tabular parallel to a pair of faces of this prism (developed more than the other pair), or parallel to *c* {001}.

Ten excellent small and perfectly transparent crystals of this magnificent bluish emerald-green salt were measured, selected from six different crops. The results are shown in the accompanying table of angles.

The crystals were of the two types illustrated in figs. 1 and 2.

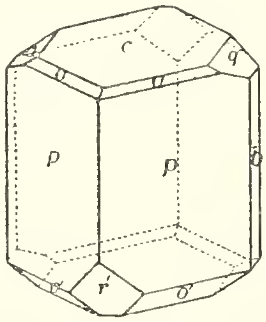

Fig. 1.

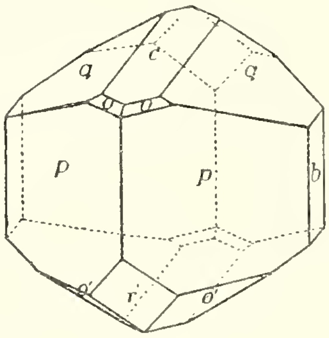

Fig. 2.

The characteristic of the first type is the predominance of the primary prism *p* {110} and the basal plane *c* {001}, with smaller faces of the clinopinakoid *b* {010}, the clinodome *q* {011}, the form *r*′{$\bar{2}$01}, and the two hemipyramids *o* {111} and *o*′{$\bar{1}$11}. The whole of the faces of the two latter forms were never found on any one crystal, and usually only one or two such faces were present. The form *r*′{$\bar{2}$01} was also very subsidiary, and on many crystals only one of the two faces was present.

---

* 'Mém. Soc. Phys. Genève,' 1885, vol. 14, p. 247.

† 'Sitz. Ber. Akad. Wiss. Wien,' 1859, vol. 34, p. 158.

INTERFACIAL Angles of Ammonium Nickel Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of	
						M. & R.	MARIGNAC.
		° ′ ° ′	° ′	° ′	′	° ′	° ′
$ac = (100):(001)$	1	—	73 4	73 3	1	72 56	—
$as = (100):(101)$	—	—	—	44 35	—	—	—
$sc = (101):(001)$	—	—	—	28 28	—	—	—
$cr' = (001):(\bar{2}01)$	8	64 56– 65 6	65 2	65 5	3	—	64 0
$cs' = (001):(\bar{1}01)$	—	—	—	39 1	—	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	26 4	—	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	1	—	41 47	41 52	5	—	—
$r'c = (\bar{2}01):(00\bar{1})$	8	114 52–115 4	114 58	114 55	3	—	—
$ap = (100):(110)$	—	—	—	35 11	—	—	—
$pp' = (110):(120)$	1	—	19 26	19 28	2	—	—
$p'b = (120):(010)$	1	—	35 18	35 21	3	—	—
$pp''' = (110):(130)$	—	—	—	29 31	—	—	—
$p'''b = (130):(010)$	—	—	—	25 18	—	—	—
$pb = (110):(010)$	28	54 39– 54 58	54 49	*	—	54 50	—
$pp = (110):(1\bar{1}0)$	16	70 8– 70 39	70 22	70 22	0	70 20	70 40
$cq = (001):(011)$	31	25 23– 25 45	25 34	*	—	25 37	25 10
$qb = (011):(010)$	35	64 17– 64 40	64 26	64 26	0	64 24	—
$ao = (100):(111)$	—	—	—	47 46	—	—	—
$oq = (111):(011)$	1	—	26 56	26 59	3	—	—
$aq = (100):(011)$	—	—	—	74 45	—	—	—
$qo' = (011):(\bar{1}11)$	1	—	35 13	35 8	5	—	32 30
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	70 7	—	—	—
$co = (001):(111)$	3	33 57– 34 0	33 58	33 58	0	—	—
$op = (111):(110)$	3	42 9– 42 15	42 12	42 15	3	—	—
$cp = (001):(110)$	38	76 1– 76 25	76 13	*	—	76 7	77 0
$po' = (110):(11\bar{1})$	19	58 28– 58 50	58 37	58 39	2	58 29	—
$o'c = (11\bar{1}):(00\bar{1})$	19	44 59– 45 19	45 9	45 8	1	45 4	44 0
$bn = (010):(121)$	—	—	—	54 57	—	—	—
$no = (121):(111)$	—	—	—	15 43	—	—	—
$bo = (010):(111)$	2	70 38– 70 39	70 39	70 40	1	—	—
$os = (111):(101)$	—	—	—	19 20	—	—	—
$bo' = (010):(\bar{1}11)$	7	65 3– 65 10	65 7	65 8	1	—	—
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 52	—	—	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	3	49 44– 49 50	49 47	49 44	3	—	50 30
$sq = (101):(011)$	—	—	—	37 32	—	—	—
$qp = (011):(\bar{1}10)$	32	87 51– 88 14	88 6	88 4	2	—	—
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 24	—	—	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	33	91 44– 92 9	91 55	91 56	1	—	—
$s'q = (\bar{1}01):(011)$	—	—	—	45 30	—	—	—
$qn = (011):(121)$	—	—	—	26 15	—	—	—
$np = (121):(110)$	—	—	—	36 8	—	—	—
$qp = (011):(110)$	35	62 14– 62 32	62 24	62 23	1	—	—
$ps' = (110):(10\bar{1})$	—	—	—	72 7	—	—	—
$pq = (110):(0\bar{1}\bar{1})$	36	117 23–117 44	117 36	117 37	1	—	—
$r'o' = (\bar{2}01):(\bar{1}11)$	11	35 21– 35 33	35 26	35 25	1	35 28	—
$o'p = (\bar{1}11):(110)$	15	91 52– 92 10	92 3	92 5	2	—	—
$pr' = (110):(20\bar{1})$	19	52 24– 52 49	52 34	52 30	4	52 24	52 30
Total number of measurements .	407						

In type 2, the $q\ \{011\}$ faces were larger, and the $c\ \{001\}$ faces relatively smaller and often reduced to narrow strips. The $r'\{\bar{2}01\}$ faces were also somewhat more prominent, and more of the faces of $o\ \{111\}$ and $o'\{\bar{1}11\}$ were developed.

The *c* and *p* faces in many crops were affected by striation, but those crystals selected for measurement were wonderfully free from this defect, and several of the crystals measured were practically perfect, yielding brilliant single images of the signal throughout, offering no trace of ambiguity as to the position of the faces. The contact face (that parallel to the bottom of the crystallising vessel) was either *c* or *p*.

The next table affords a comparison of the axial angles and axial ratios of the four salts containing nickel. The axial angle of the ammonium salt is almost identical with that of the cæsium salt. The values of the axial ratios of the ammonium salt clearly indicate the existence of isomorphism between this salt and the three salts containing the alkali metals.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium nickel sulphate . .	105° 0′	0·7379 : 1 : 0·5020
Rubidium ,, ,, . .	106° 3′	0·7350 : 1 : 0·5022
Ammonium ,, ,, . .	106° 57′	0·7373 : 1 : 0·5000
Cæsium ,, ,, . .	107° 2′	0·7270 : 1 : 0·4984

The next table affords a comparison of the morphological angles of the four salts.

COMPARISON of the Interfacial Angles.

Angle.	KNi sulphate.	RbNi sulphate.	CsNi sulphate.	AmNi sulphate.
	° ′	° ′	° ′	° ′
$ac = (100) : (001)$	75 0	73 57	72 58	73 3
$as = (100) : (101)$	45 48	45 4	44 21	44 35
$sc = (101) : (001)$	29 12	28 53	28 37	28 28
$cr' = (001) : (\bar{2}01)$	63 44	64 36	65 28	65 5
$cs' = (001) : (\bar{1}01)$	38 33	38 57	39 22	39 1
$s'r' = (\bar{1}01) : (\bar{2}01)$	25 11	25 39	26 6	26 4
$r'a = (\bar{2}01) : (\bar{1}00)$	41 16	41 27	41 34	41 52
$ap = (100) : (110)$	35 29	35 17	34 48	35 11
$pp' = (110) : (120)$	19 28	19 28	19 28	19 28
$p'b = (120) : (010)$	35 3	35 15	35 44	35 21
$pb = (110) : (010)$	54 31	54 43	55 12	54 49
$cq = (001) : (011)$	25 52	25 44	25 28	25 34
$qb = (011) : (010)$	64 8	64 16	64 32	64 26

COMPARISON of the Interfacial Angles (continued).

Angle.	KNi sulphate.	RbNi sulphate.	CsNi sulphate.	AmNi sulphate.
	° ′	° ′	° ′	° ′
$ao = (100):(111)$	48 59	48 16	47 32	47 46
$oq = (111):(011)$	27 33	27 19	27 8	26 59
$aq = (100):(011)$	76 32	75 35	74 40	74 45
$qo' = (011):(\bar{1}11)$	34 46	35 5	35 31	35 8
$o'a = (\bar{1}11):(\bar{1}00)$	68 42	69 20	69 49	70 7
$co = (001):(111)$	34 46	34 25	34 0	33 58
$op = (111):(110)$	43 4	42 32	42 5	42 15
$cp = (001):(110)$	77 50	76 57	76 5	76 13
$po' = (110):(11\bar{1})$	57 26	57 57	58 31	58 39
$o'c = (11\bar{1}):(00\bar{1})$	44 44	45 6	45 24	45 8
$bo = (010):(111)$	70 12	70 25	70 48	70 40
$os = (111):(101)$	19 48	19 35	19 12	19 20
$bo' = (010):(\bar{1}11)$	65 17	65 11	65 15	65 8
$o's' = (\bar{1}11):(\bar{1}01)$	24 43	24 49	24 45	24 52
$sq = (101):(011)$	38 13	37 56	37 35	37 32
$qp = (011):(\bar{1}10)$	86 22	87 17	88 23	88 4
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 25	54 47	54 2	54 24
$s'q = (\bar{1}01):(011)$	45 17	45 32	45 44	45 30
$qp = (011):(110)$	63 43	63 0	62 27	62 23
$ps' = (110):(10\bar{1})$	71 0	71 28	71 49	72 7
$r'o' = (\bar{2}01):(\bar{1}11)$	34 43	35 6	35 22	35 25
$o'p = (\bar{1}11):(110)$	93 1	92 38	92 32	92 5
$pr' = (110):(20\bar{1})$	52 16	52 16	52 6	52 30

The average and maximum changes of angle for the various replacements of one alkali base by another are given in the small table which follows.

DOUBLE Sulphates containing Nickel.

Replacement.	Average change.	Maximum change.
	′	′ ° ′
K by Rb	27	63 = 1 3
K by Cs	54	122 = 2 2
K by NH_4	49	117 = 1 57

The average and maximum changes of angle when potassium is replaced by ammonium are very nearly the same as occur when potassium is replaced by cæsium, and are twice as great as when potassium is replaced by rubidium.

Of the 36 angles compared, 33 show differences on replacing potassium by ammonium in the same direction as when rubidium or cæsium are introduced instead of potassium, the only three exceptions being when the differences are very minute. In 32 of the 33 cases the changes are greater than when rubidium is introduced, and in 11 cases they exceed the effect produced by introducing cæsium for potassium.

Cleavage.—There is a good cleavage parallel to $r'\{\bar{2}01\}$, as usual in this series. Also a good cleavage was found parallel to $b\,\{010\}$.

Volume.

Relative Density.—Five determinations of specific gravity by the immersion method, using methylene iodide and benzene as the immersion liquid, gave the following results:—

I.	Density for	18°·9/4° . . .	1·9240	For 20°/4° . . .	1·9238
II.	,,	19°·4/4° . . .	1·9238	,, 20°/4° . . .	1·9237
III.	,,	18°·8/4° . . .	1·9228	,, 20°/4° . . .	1·9226
IV.	,,	18°·2/4° . . .	1·9222	,, 20°/4° . . .	1·9219
V.	,,	19°·1/4° . . .	1·9219	,, 20°/4° . . .	1·9217
				Mean . . .	1·9227

The value accepted for 20°/4° is therefore **1·923**.

Perrot[*] obtained the value 1·92 (three individual values 1·920, 1·920, and 1·927).

Molecular Volume.—$\frac{M}{d} = \frac{392{\cdot}12}{1{\cdot}923} = 203{\cdot}91$. Perrot gives 205.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6{\cdot}1426 : 8{\cdot}3312 : 4{\cdot}1656.$$

Redeterminations of Densities of Potassium, Rubidium, and Cæsium Nickel Sulphates.—These were carried out in order to render all results involving the molecular volumes of the four salts strictly comparable, the same immersion liquid being used under like conditions.

In earlier density determinations made with these salts the pyknometer method was employed.

Potassium Nickel Sulphate, $K_2Ni\,(SO_4)_2 \,.\, 6H_2O$.

I.	Density for	19°·0/4° . . .	2·2363	For 20°/4° . . .	2·2361
II.	,,	17°·7/4° . . .	2·2378	,, 20°/4° . . .	2·2373
III.	,,	18°·1/4° . . .	2·2357	,, 20°/4° . . .	2·2353
IV.	,,	19°·6/4° . . .	2·2374	,, 20°/4° . . .	2·2373
				Mean . . .	2·2365

The value accepted for 20°/4° is **2·237**.

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[*] 'Arch. des Sciences phys. et nat., Genève,' 1891, 23. 'Dissertation, Genève,' 1890, 47.

Rubidium Nickel Sulphate, $Rb_2Ni(SO_4)_2 . 6H_2O$.

I.	Density for	17°·8/4° . . .	2·5857	For 20°/4° . . .	2·5851
II.	„	17°·2/4° . . .	2·5854	„ 20°/4° . . .	2·5847
III.	„	17°·5/4° . . .	2·5867	„ 20°/4° . . .	2·5861
IV.	„	17°·6/4° . . .	2·5886	„ 20°/4° . . .	2·5880
				Mean . . .	2·5860

The value accepted for 20°/4° is **2·586**.

Cæsium Nickel Sulphate, $Cs_2Ni(SO_4)_2 . 6H_2O$.

I.	Density for	19°·1/4° . . .	2·8720	For 20°/4° . . .	2·8717
II.	„	18°·0/4° . . .	2·8753	„ 20°/4° . . .	2·8747
III.	„	19°·2/4° . . .	2·8706	„ 20°/4° . . .	2·8704
IV.	„	19°·6/4° . . .	2·8730	„ 20°/4° . . .	2·8729
				Mean . . .	2·8724

The value accepted for 20°/4° is **2·872**.

The former pyknometer values obtained for the three salts were respectively 2·233, 2·583, and 2·865. The higher values now obtained are doubtless very near the truth, the error of the pyknometer method being on the side of lowness, due to inevitable mother-liquor inclusions, whereas the immersion method affords the result for the most cavity-free crystal.

In the next table the volume constants of the four nickel-containing salts are compared. It shows that the molecular volume and topic axial ratios of the ammonium salt are close to those of the rubidium salt; the molecular volume is half a unit higher, the χ and ψ ratios are also slightly higher and the ω ratio very slightly lower.

VOLUME Constants of the Nickel Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				χ : ψ : ω
KNi sulphate . .	433·96	2·237	193·99	6·0170 : 8·1542 : 4·0934
RbNi „ . .	526·06	2·586	203·43	6·1065 : 8·3081 : 4·1723
NH_4Ni „ . .	392·12	1·923	203·91	6·1426 : 8·3312 : 4·1656
CsNi „ . .	620·06	2·872	215·90	6·2097 : 8·5416 : 4·2572

Optics.

Orientation of the Optical Ellipsoid.—The plane of the optic axes is the symmetry plane b {010}. The double refraction is of positive sign, so that the first median line corresponds to the refractive index γ and the second median line to α.

Extinction determinations with two sections parallel to the symmetry plane afforded the following results:—

Inclination of 2M.L. *from normal to* c {001}.

Plate 1. . . . . . 11° 28′ Plate 2. . . . . . 12° 2′
Mean . . . 11° 45′

The direction is behind the normal, towards the vertical axis c.

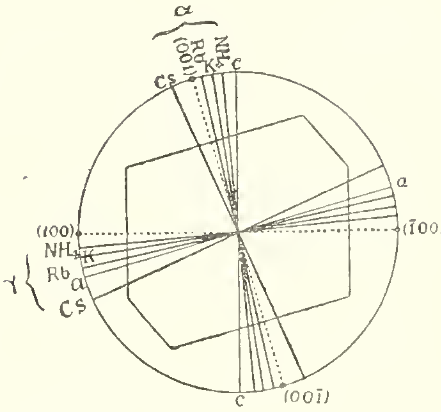

Fig. 3.

Murmann and Rotter found for this angle 10° 58′, and Senarmont 12° 1′.

As the axial angle ac is 73° 3′, this 2M.L. extinction direction is 5° 12′ in front of the vertical axis c, and the first median line is 11° 45′ from the inclined axis a, both extinction directions in the symmetry plane thus lying in the obtuse axial angle ac.

The next table shows the positions of the α extinction direction in all four nickel salts, and fig. 3 illustrates them graphically.

Inclinations of α *extinctions of* Ni *salts in front of axis* c.

(2M.L. for Am, K, and Rb salts, 1M.L. for Cs salt.)

AmNi Sulphate	5° 12′	RbNi Sulphate	12° 38′
KNi ,,	8° 42′	CsNi ,,	24° 7′

The position of the ammonium salt ellipsoid is such that its α axis lies nearest to the c axis, and the ellipsoid rotates as the potassium, rubidium, and cæsium salts are successively reached, further and further from this position, the rotation following the order of the atomic weights of the three alkali metals.

Refractive Indices.—Six 60°-prisms were ground by means of the author's cutting and grinding goniometer,* each to afford two indices directly, and the results are

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* A new crystal-grinding goniometer on the Goldschmidt two-circle principle has recently been described by F. E. Wright ('Journ. Washington Acad. of Sciences,' 1915, 5, 35). In its description a mere passing mention is made of the very efficient instrument which the author (Tutton) described in the year 1899 ('Phil. Trans. Roy. Soc.,' A, 1899, 192, 457; 'Zeitschr. für Kryst.,' 1899, 31, 458; 'Crystallography and Practical Crystal Measurement,' 1911, p. 682), and which has been used in all his investigations during the past 16 years, over a thousand section-plates and prisms having been most accurately prepared with its aid, truly orientated and plane surfaced. This instrument is capable of achieving all that the new Wright instrument is described as accomplishing, and much more besides. The use of a second circle cannot add to rigidity, and the author infinitely prefers the most rigid one-circle principle. After 16 years of hard service the author's cutting and grinding goniometer is as efficient and accurate as when first constructed by Messrs. Troughton and Simms.

given in the next table. This is followed by another table, in which the refractive indices of the four nickel-containing salts are compared.

Murmann and Rotter obtained indirectly the values $\alpha = 1{\cdot}489$, $\beta = 1{\cdot}498$, and $\gamma = 1{\cdot}508$ for the middle of the spectrum.

There is a considerable amount of absorption by this green salt at the red end of the spectrum, but the electric arc, used as a source of light with the author's spectroscopic monochromatic illuminator,* affords ample light for the observations in Li and C light.

Refractive Indices of Ammonium Nickel Sulphate.

Light.	α.	β.	γ.
Li	1·4916	1·4975	1·5046
C	1·4921	1·4980	1·5051
Na	1·4949	1·5007	1·5081
Tl	1·4976	1·5037	1·5110
Cd	1·4993	1·5052	1·5125
F	1·5007	1·5069	1·5142
G	1·5060	1·5123	1·5196

Mean of α, β, and γ for Na light = 1·5012.

α = Vibration direction parallel to second median line, 5° 12′ in front of axis c.

β = ,, ,, ,, symmetry axis b.

γ = ,, ,, ,, first median line.

General Formula for the intermediate refractive index β, corrected to a vacuum (correction +0·0004):—

$$\beta = 1{\cdot}4873 + \frac{472\,952}{\lambda^2} + \frac{212\,960\,000\,000}{\lambda^4} + \ldots$$

The α indices are also reproduced very closely by the formula if the constant 1·4873 is diminished by 0·0060, and the γ indices if the constant is increased by 0·0073.

Observations at 70° indicate that the refractive indices of ammonium nickel sulphate are diminished by about 0·0018° (for α) to 0·0022° (for γ) for 55° rise of temperature.

The comparative table shows that the refractive indices of ammonium nickel sulphate are just slightly higher than those of the analogous rubidium salt, and not nearly so high as those of the cæsium salt. This is also clearly apparent as regards the mean refractive index given at the foot of the table. As regards double refraction, the ammonium salt occupies a similar position between the rubidium and cæsium salts and much nearer to the rubidium one; as this property of double refraction diminishes

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* 'Crystallography and Practical Crystal Measurement,' 1911, p. 698.

Comparison of the Refractive Indices.

Index.	Light	KNi sulphate	RbNi sulphate.	NH_4Ni sulphate.	CsNi sulphate.
α	Li	1·4809	1·4868	1·4916	1·5061
	C	1·4813	1·4872	1·4921	1·5065
	Na	1·4836	1·4895	1·4949	1·5087
	Tl	1·4860	1·4920	1·4976	1·5112
	F	1·4889	1·4949	1·5007	1·5146
	G	1·4933	1·4996	1·5060	1·5192
β	Li	1·4889	1·4933	1·4975	1·5100
	C	1·4893	1·4937	1·4980	1·5104
	Na	1·4916	1·4961	1·5007	1·5129
	Tl	1·4941	1·4987	1·5037	1·5154
	F	1·4972	1·5017	1·5069	1·5187
	G	1·5015	1·5062	1·5123	1·5235
γ	Li	1·5022	1·5023	1·5046	1·5133
	C	1·5026	1·5027	1·5051	1·5137
	Na	1·5051	1·5052	1·5081	1·5162
	Tl	1·5077	1·5078	1·5110	1·5189
	F	1·5109	1·5110	1·5142	1·5221
	G	1·5153	1·5156	1·5196	1·5266
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4934	1·4969	1·5012	1·5126
Double refraction, $Na_{\gamma-\alpha}$		0·0215	0·0157	0·0132	0·0075

with rise of atomic weight of the alkali metal, the value is less than that for the rubidium salt.

Axial Ratios of the Optical Indicatrix.

	$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KNi sulphate . . .	0·9946 : 1 : 1·0091	0·9946 : 1 : 1·0091
RbNi ,, . . .	0·9956 : 1 : 1·0061	0·9986 : 1·0030 : 1·0091
NH_4Ni ,, . . .	0·9961 : 1 : 1·0049	1·0022 : 1·0061 : 1·0111
CsNi ,, . . .	0·9972 : 1 : 1·0022	1·0115 : 1·0143 : 1·0165

Axial Ratios of the Optical Velocity Ellipsoid.

	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$
KNi sulphate . . .	1·0054 : 1 : 0·9910	1·0054 : 1 : 0·9910
RbNi ,, . . .	1·0044 : 1 : 0·9940	1·0014 : 0·9970 : 0·9910
NH_4Ni ,, . . .	1·0039 : 1 : 0·9951	0·9978 : 0·9939 : 0·9891
CsNi ,, . . .	1·0028 : 1 : 0·9978	0·9887 : 0·9859 : 0·9838

Axial Ratios of the Optical Ellipsoid.—These have been calculated for ammonium nickel sulphate for either form of ellipsoid; the values are given in the accompanying table, and are compared with the values for the three analogous salts of the alkali metals. The first series (on the left) shows the ratios when the β-axis of each salt is taken as 1, and the second (right hand) series when the β-axis of the potassium salt is taken = 1; this second series thus shows the effect on the optical ellipsoid of replacing one alkali base by another. In both series the position of the ammonium salt is between the rubidium and cæsium salts, and much nearer to the former.

Molecular Optical Constants.—These have been calculated with the aid of the densities as determined by the immersion method, both for the ammonium salt now under discussion, and for the potassium, rubidium, and cæsium salts, and the results are set forth comparatively in the next three tables.

The specific refraction and dispersion of ammonium nickel sulphate are considerably higher than those of the alkali-metal salts. The molecular dispersion is slightly higher than that of the cæsium salt. The molecular refraction, whether calculated by the formula of LORENZ, or by that of GLADSTONE and DALE, is very close to (just higher than) that for the rubidium salt. The mean molecular refraction shows this very succinctly.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.						Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmNi . . .	0·1509	0·1524	0·1543	0·1545	0·1561	0·1580	0·0036	0·0037	0·0037
KNi	0·1273	0·1290	0·1321	0·1300	0·1318	0·1349	0·0027	0·0028	0·0028
RbNi . . .	0·1113	0·1125	0·1143	0·1137	0·1149	0·1167	0·0024	0·0024	0·0024
CsNi . . .	0·1035	0·1042	0·1048	0·1057	0·1064	0·1070	0·0022	0·0022	0·0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.						Molecular dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KNi sulphate	55·23	56·00	57·31	56·41	57·20	58·53	1·18	1·20	1·22
RbNi ,,	58·53	59·19	60·10	59·79	60·46	61·40	1·26	1·27	1·30
AmNi ,,	59·17	59·77	60·49	60·58	61·22	61·95	1·41	1·45	1·46
CsNi ,,	64·20	64·61	64·97	65·55	66·00	66·34	1·35	1·39	1·37

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KNi sulphate	93·37	94·92	97·50	95·26
RbNi ,, ...	99·11	100·43	102·26	100·60
AmNi ,, ...	100·34	101·55	103·00	101·63
CsNi ,, ...	109·35	110·19	110·91	110·15

Optic Axial Angle.—Three pairs of section plates were ground perpendicular to the first and second median lines. The optic axial angle is so large as to be invisible in air. The next table affords the results of the measurements of $2H_a$ and $2H_o$ in monobromonaphthalene, the interference figures in which are very well defined.

MURMANN and ROTTER obtained 86° 26′ for the true angle $2V_a$, for the middle of the spectrum.

Dispersion of the Median Lines.—The inclined dispersion of the median lines is small. Measurements in toluene, the refractive index of which (1·4955) is slightly lower, and in benzene, which possesses a slightly higher index (1·5027), indicated that the dispersion is such that the first median line is nearer by 8 minutes to the axis a for red C-hydrogen light than for greenish-blue F-hydrogen light.

Ammonium Nickel Sulphate.

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	76 33	1*a*	82 35	86 23	86 27
	2	76 26	2*a*	82 18	86 28	
	3	76 32	3*a*	82 20	86 31	
C	1	76 30	1*a*	82 31	86 24	86 28
	2	76 23	2*a*	82 13	86 28	
	3	76 29	3*a*	82 15	86 32	
Na	1	76 8	1*a*	81 55	86 30	86 33
	2	76 7	2*a*	81 50	86 32	
	3	76 10	3*a*	81 45	86 36	
Tl	1	75 51	1*a*	81 29	86 34	86 37
	2	75 50	2*a*	81 23	86 36	
	3	75 50	3*a*	81 19	86 40	
Cd	1	75 42	1*a*	81 11	86 38	86 40
	2	75 39	2*a*	81 5	86 40	
	3	75 38	3*a*	81 0	86 42	
F	1	75 33	1*a*	80 56	86 42	86 43
	2	75 27	2*a*	80 50	86 42	
	3	75 26	3*a*	80 45	86 44	

A comparison of the optic axial angles of the four salts containing nickel, instituted in the next table, shows that the angle for the ammonium salt is close to that of the cæsium salt, being slightly lower than the latter. It has to be remembered that cæsium nickel sulphate is (by exception in the series) of negative double refraction, so that the first median line is, in this case, the α axis of the indicatrix ellipsoid, instead of (as usual in the series) the γ axis.

Optic Axial Angles $2V_a$ of the Nickel Group.

	KNi sulphate.	RbNi sulphate.	AmNi sulphate.	CsNi sulphate.
	° ′	° ′	° ′	° ′
Li	75 21	82 5	86 27	87 15
C	75 19	82 4	86 28	87 17
Na	75 16	82 0	86 33	87 21
Tl	75 13	81 56	86 37	87 29
F	75 9	81 48	86 43	87 40

Ammonium Cobalt Sulphate $(NH_4)_2\,Co\,(SO_4)_2 \,.\, 6H_2O$.

Morphology.

The only crystallographic investigation of this salt hitherto made is that of MARIGNAC (*loc. cit.*). The values of the angles observed by him are quoted in the last column of the table of angles.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—

$a : b : c = 0·7386 : 1 : 0·4975$. Values of MARIGNAC, $0·7392 : 1 : 0·4985$.

Axial Angle.—$\beta = 107° \; 2'$. Value of MARIGNAC, $106° \; 56'$.

Forms Observed.—$a\,\{100\}$, $b\,\{010\}$, $c\,\{001\}$, $p\,\{110\}$, $q\,\{011\}$, $r'\{\bar{2}01\}$, $o\,\{111\}$, $o'\{\bar{1}11\}$.

Habit.—Short prismatic parallel $p\,\{110\}$, often with narrower c faces and larger q faces than in the nickel salt; or more or less tabular parallel to a pair of faces of this prism $p\,\{110\}$ predominatingly grown, or to $c\,\{001\}$.

This is one of the finest salts of the series, the crystals being of a ruby or red-currant red colour. The crystals of several of the numerous crops obtained were composed of completely transparent well-developed individuals, having absolutely plane faces yielding brilliant single images of the signal of unusual perfection. Ten superb crystals were measured, selected from five different crops. The results are shown in the table of angles. A typical crystal is shown in fig. 4, and fig. 2, representing a crystal of ammonium nickel sulphate, is equally typical of many crops of the cobalt analogue. Both are of the short prismatic type, but not infrequently

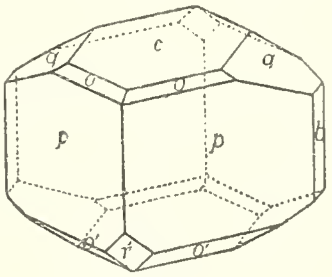

Fig. 4.

INTERFACIAL Angles of Ammonium Cobalt Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of MARIGNAC.
		° ′ ° ′	° ′	° ′	′	° ′
ac = $(100):(001)$	—	—	—	72 58	—	73 4
as = $(100):(101)$	—	—	—	44 43	—	—
sc = $(101):(001)$	—	—	—	28 15	—	—
cr′ = $(001):(\bar{2}01)$	17	64 37– 64 59	64 52	64 46	6	64 48
cs′ = $(001):(\bar{1}01)$	—	—	—	38 41	—	—
s′r′ = $(\bar{1}01):(\bar{2}01)$	—	—	—	26 5	—	—
r′a = $(\bar{2}01):(\bar{1}00)$	—	—	—	42 16	—	—
r′c = $(\bar{2}01):(00\bar{1})$	16	115 2–115 21	115 8	115 14	6	—
ap = $(100):(110)$	—	—	—	35 14	—	—
pp′ = $(110):(120)$	—	—	—	19 28	—	—
p′b = $(120):(010)$	—	—	—	35 18	—	—
pp‴ = $(110):(130)$	—	—	—	29 30	—	—
p‴b = $(130):(010)$	—	—	—	25 16	—	—
pb = $(110):(010)$	40	54 38– 54 52	54 46	*	—	—
pp = $(110):(1\bar{1}0)$	20	70 23– 70 33	70 28	70 28	0	70 32
cq = $(001):(011)$	31	25 12– 25 39	25 26	*	—	25 15
qb = $(011):(010)$	33	64 27– 64 52	64 34	64 34	0	—
ao = $(100):(111)$	—	—	—	47 52	—	—
oq = $(111):(011)$	4	26 41– 26 51	26 47	26 47	0	26 47
aq = $(100):(011)$	1	—	74 29	74 39	10	—
qo′ = $(011):(\bar{1}11)$	5	34 54– 35 6	35 2	34 57	5	34 55
o′a = $(\bar{1}11):(\bar{1}00)$	1	—	70 33	70 24	9	—
co = $(001):(111)$	9	33 42– 33 52	33 46	33 45	1	33 40
op = $(111):(110)$	9	42 18– 42 29	42 22	42 24	2	—
cp = $(001):(110)$	40	75 55– 76 24	76 9	*	—	76 14
po′ = $(110):(11\bar{1})$	16	58 40– 58 59	58 52	58 56	4	—
o′c = $(11\bar{1}):(00\bar{1})$	16	44 50– 45 25	44 57	44 55	2	44 54
bn = $(010):(121)$	—	—	—	55 1	—	—
no = $(121):(111)$	—	—	—	15 42	—	—
bo = $(010):(111)$	7	70 35– 70 46	70 41	70 43	2	—
os = $(111):(101)$	—	—	—	19 17	—	—
oo = $(111):(1\bar{1}1)$	1	—	38 38	38 34	4	38 39
bo′ = $(010):(\bar{1}11)$	7	65 6– 65 20	65 10	65 11	1	—
o′s′ = $(\bar{1}11):(\bar{1}01)$	—	—	—	24 49	—	—
o′o′ = $(\bar{1}11):(\bar{1}\bar{1}1)$	1	—	49 42	49 38	4	49 20
sq = $(101):(011)$	—	—	—	37 18	—	—
qp = $(011):(\bar{1}10)$	37	88 2– 88 29	88 12	88 11	1	—
ps = $(\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 31	—	—
pq = $(\bar{1}10):(0\bar{1}\bar{1})$	38	91 27– 91 57	91 47	91 49	2	—
s′q = $(\bar{1}01):(011)$	—	—	—	45 11	—	—
qn = $(011):(121)$	—	—	—	26 6	—	—
np = $(121):(110)$	—	—	—	36 15	—	—
qp = $(011):(110)$	36	62 7– 62 28	62 21	62 21	0	—
ps′ = $(110):(10\bar{1})$	—	—	—	72 28	—	—
pq = $(110):(0\bar{1}\bar{1})$	36	117 29–117 52	117 40	117 39	1	—
r′o′ = $(\bar{2}01):(\bar{1}11)$	17	35 9– 35 37	35 21	35 23	2	35 28
o′p = $(\bar{1}11):(110)$	18	91 44– 92 5	91 54	91 48	6	—
pr′ = $(110):(20\bar{1})$	36	52 36– 52 52	52 43	52 49	6	52 40
Total number of measurements . .	492					

the prism is relatively longer than is shown in the two figures. In the great majority of crops prepared the type was that of fig. 4, or of the same elongated vertically, the faces of the basal plane *c* {001} predominating at the terminations. But in several of the crops the *c* faces were relatively narrower and the faces of *q* {011} proportionately larger, as shown in fig. 2. In all the crops the prism faces *p* {110} were always important, and indeed usually predominated. The two faces of the clinopinakoid *b* {010} were often well developed, although many crops showed these faces only as strips, and not uncommonly they were either entirely absent or mere lines. The faces of the orthopinakoid $r' \{\bar{2}01\}$ were usually very subordinate, as shown in the figure. The two hemipyramids *o* {111} and $o' \{\bar{1}11\}$ were usually represented by some of their faces, and the latter form often by all its faces, although small. The orthopinakoid *a* {100} was only very rarely developed to a measurable extent.

The next three tables compare the morphological constants of the four salts containing cobalt. The first of these shows that the axial angle β of ammonium cobalt sulphate is very close to that of cæsium cobalt sulphate, and that the axial ratios of the ammonium salt are very clearly such as place that salt in the same isomorphous series as the three cobalt salts containing the alkali metals.

The angular comparisons instituted in the second table are supplemented by a further short table showing the average and maximum changes of angle which occur when potassium is replaced by the other three alkali bases. These changes are seen to be nearly the same for the ammonium and cæsium replacements, and these again are twice as great as the average and maximum changes of angle when rubidium is introduced instead of potassium. A critical analysis of the comparative table of angles also shows that of the 36 angles compared 32 show changes, when ammonium replaces potassium, in the same direction as when the latter is replaced by the other two alkali metals, and the only four exceptions are in cases where the changes are very minute. Of the 32, 29 show larger changes than for the rubidium replacement, and 11 show even larger changes than for the cæsium replacement.

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium cobalt sulphate	104° 55′	0·7404 : 1 : 0·5037
Rubidium ,, ,,	106° 1′	0·7391 : 1 : 0·5011
Ammonium ,, ,,	107° 2′	0·7386 : 1 : 0·4975
Cæsium ,, ,,	107° 8′	0·7270 : 1 : 0·4968

COMPARISON of the Interfacial Angles.

Angle.	KCo sulphate.	RbCo sulphate.	CsCo sulphate.	AmCo sulphate.
	° ′	° ′	° ′	° ′
$ac = (100):(001)$	75 5	73 59	72 52	72 58
$as = (100):(101)$	45 53	45 11	44 20	44 43
$sc = (101):(001)$	29 12	28 48	28 32	28 15
$cr' = (001):(\bar{2}01)$	63 38	64 24	65 24	64 46
$cs' = (001):(\bar{1}01)$	38 29	38 47	39 15	38 41
$s'r' = (\bar{1}01):(\bar{2}01)$	25 9	25 37	26 9	26 5
$r'a = (\bar{2}01):(\bar{1}00)$	41 17	41 37	41 44	42 16
$ap = (100):(110)$	35 37	35 21	34 48	35 14
$pp' = (110):(120)$	19 28	19 28	19 28	19 28
$p'b = (120):(010)$	34 55	35 11	35 44	35 18
$pb = (110):(010)$	54 23	54 39	55 12	54 46
$cq = (001):(011)$	25 55	25 43	25 24	25 26
$qb = (011):(010)$	64 5	64 17	64 36	64 34
$ao = (100):(111)$	49 6	48 23	47 30	47 52
$oq = (111):(011)$	27 31	27 13	27 4	26 47
$aq = (100):(011)$	76 37	75 36	74 34	74 39
$qo' = (011):(\bar{1}11)$	34 41	34 59	35 26	34 57
$o'a = (\bar{1}11):(\bar{1}00)$	68 42	69 25	70 0	70 24
$co = (001):(111)$	34 50	34 20	33 54	33 45
$op = (111):(110)$	43 5	42 40	42 6	42 24
$cp = (001):(110)$	77 55	77 0	76 0	76 9
$po' = (110):(11\bar{1})$	57 22	58 3	58 42	58 56
$o'c = (11\bar{1}):(00\bar{1})$	44 43	44 57	45 18	44 55
$bo = (010):(111)$	70 7	70 26	70 52	70 43
$os = (111):(101)$	19 53	19 34	19 8	19 17
$bo' = (010):(\bar{1}11)$	65 13	65 12	65 17	65 11
$o's' = (\bar{1}11):(\bar{1}01)$	24 47	24 48	24 43	24 49
$sq = (101):(011)$	38 16	37 51	37 29	37 18
$qp = (011):(\bar{1}10)$	86 12	87 14	88 29	88 11
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 32	54 55	54 2	54 31
$s'q = (\bar{1}01):(011)$	45 15	45 23	45 37	45 11
$qp = (011):(110)$	63 43	63 0	62 24	62 21
$ps' = (110):(10\bar{1})$	71 2	71 37	71 59	72 28
$r'o' = (\bar{2}01):(\bar{1}11)$	34 44	35 4	35 22	35 23
$o'p = (\bar{1}11):(110)$	92 55	92 30	92 25	91 48
$pr' = (110):(20\bar{1})$	52 21	52 26	52 13	52 49

DOUBLE Sulphates containing Cobalt.

Replacement.	Average change.	Maximum change.
	′	′ ° ′
K by Rb	27	66 = 1 6
K by Cs	56	137 = 2 17
K by NH_4	52	127 = 2 7

Cleavage.—The common cleavage of the series parallel $r\ \{\bar{2}01\}$ is well developed in this salt. No trace of the $b\ \{010\}$ cleavage found on the nickel ammonium salt was discoverable on the cobalt salt.

Volume.

Relative Density.—Five determinations by the immersion method gave the following results :—

I.	Density for	16°·8/4° . . .	1·9000	For	20°/4° . . .	1·8994
II.	,,	17°·4/4° . . .	1·9006	,,	20°/4° . . .	1·9001
III.	,,	16°·2/4° . . .	1·9037	,,	20°/4° . . .	1·9030
IV.	,,	16°·3/4° . . .	1·9016	,,	20°/4° . . .	1·9009
V.	,,	16°·8/4° . . .	1·9014	,,	20°/4° . . .	1·9008
					Mean . . .	1·9008

The value accepted for 20°/4° is **1·901**.

Perrot (*loc. cit.*) records three determinations of the density of this salt, the values obtained being 1·895, 1·892, and 1·862, and gives as his accepted mean 1·88.

Molecular Volume.— $\frac{M}{d} = \frac{392·37}{1·901} = 206·40$. Perrot gives 210.

Molecular Distance Ratios (*topic axial ratios*).—

$$\chi : \psi : \omega = 6·1860 : 8·3753 : 4·1667.$$

Redeterminations of Densities of Alkali-Metal-Cobalt Salts.

Potassium Cobalt Sulphate, $K_2Co\,(SO_4)_2 \,.\, 6H_2O$.

I.	Density for	15°·3/4° . . .	2·2196	For	20°/4° . . .	2·2186
II.	,,	15°·1/4° . . .	2·2203	,,	20°/4° . . .	2·2192
III.	,,	15°·2/4° . . .	2·2175	,,	20°/4° . . .	2·2164
IV.	,,	15°·7/4° . . .	2·2211	,,	20°/4° . . .	2·2201
V.	,,	16°·9/4° . . .	2·2213	,,	20°/4° . . .	2·2206
					Mean . . .	2·2190

The value accepted for 20°/4° is **2·219**.

Rubidium Cobalt Sulphate, $Rb_2Co\,(SO_4)_2 \,.\, 6H_2O$.

I.	Density for	13°·6/4° . . .	2·5676	For	20°/4° . . .	2·5660
II.	,,	15°·1/4° . . .	2·5679	,,	20°/4° . . .	2·5666
III.	,,	15°·0/4° . . .	2·5684	,,	20°/4° . . .	2·5671
IV.	,,	15°·2/4° . . .	2·5676	,,	20°/4° . . .	2·5664
					Mean . . .	2·5665

The value accepted for 20°/4° is **2·567**.

Cæsium Cobalt Sulphate, $Cs_2Co(SO_4)_2 . 6H_2O$.

I.	Density for 16°·7/4°	. . . 2·8468	For 20°/4°	. . .	2·8459
II.	,, 16°·7/4°	. . . 2·8444	,, 20°/4°	. . .	2·8435
III.	,, 17°·7/4°	. . . 2·8439	,, 20°/4°	. . .	2·8432
IV.	,, 18°·1/4°	. . . 2·8436	,, 20°/4°	. . .	2·8431
			Mean	. . .	2·8439

The value accepted for 20°/4° is 2·844.

The former pyknometer values for potassium, rubidium, and cæsium cobalt sulphates were 2·212, 2·557, and 2·837 respectively. The new values all being higher are certainly nearer the truth.

The next table affords a comparison of the volume constants of all four cobalt-containing salts.

VOLUME Constants of the Cobalt Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				χ : ψ : ω
KCo sulphate . .	434·21	2·219	195·68	6·0405 : 8·1583 : 4·1093
RbCo ,, . .	526·31	2·567	205·03	6·1494 : 8·3201 : 4·1692
NH_4Co ,, . .	392·37	1·901	206·40	6·1860 : 8·3753 : 4·1667
CsCo ,, . .	620·31	2·844	218·11	6·2386 : 8·5814 : 4·2632

It shows that the position of the ammonium salt as regards both molecular volume and topic axial ratios is close to that of the rubidium salt; the molecular volume and the ratios χ and ψ are slightly higher, and the ratio ω slightly lower.

Optics.

Orientation of the Optical Ellipsoid.—The symmetry plane b {010} is the plane of the optic axes. The double refraction is positive, the first median line corresponding to the refractive index γ, and the second median line to α. Two section plates parallel to the symmetry plane afforded the following extinction angles :—

Inclination of 2M.L. *from normal to* c {001}.

Plate I. . . . 10° 38′ Plate II. . . . 10° 48′
Mean . . . 10° 43′.

The direction is behind the normal, towards axis c.

MURMANN and ROTTER obtained 11° 0′ for this extinction angle, and SENARMONT gives it as 12° 0′.

As the axial angle $ac = 72° 58'$, this extinction direction of the second median line is 6° 19′ in front of the vertical axis *c*, and the first median line is 10° 43′ above the axis *a*, both median lines being in the obtuse angle of the morphological axes *ac*. The positions of the optical ellipsoids of all four cobalt-containing salts are compared in the following table, and are graphically expressed in the accompanying fig. 5.

Inclinations of α Axis of Indicatrix (2M.L.) *of the Cobalt Salts in front of Axis c.*

AmCo sulphate		6° 19′
KCo	,,	10° 5′
RbCo	,,	16° 1′
CsCo	,,	26° 8′

The ammonium salt ellipsoid lies with its α axis nearest the vertical axis *c*, and the ellipsoid rotates further away from this position as ammonium is replaced by potassium, rubidium, and cæsium in turn, according to the order of the atomic weights of those alkali metals.

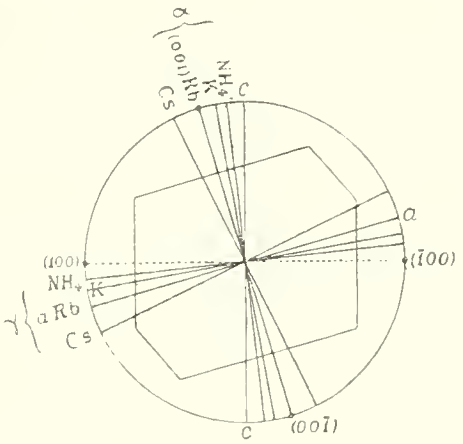

Fig. 5.

Refractive Indices.—The following table gives the results of measurements with six excellent 60°-prisms, each ground accurately to afford two indices directly, the prism edge and bisecting plane being parallel to a principal axis and principal plane of the indicatrix. There is considerable absorption in the green and blue parts of the spectrum, but the illumination of the images of the spectrometer slit for Tl, Cd and F light was quite adequate to ensure accuracy, using the electric arc with the monochromatic illuminator, as usual.

REFRACTIVE Indices of Ammonium Cobalt Sulphate.

Light.	α.	β.	γ.
Li	1·4871	1·4922	1·5001
C	1·4876	1·4927	1·5006
Na	1·4902	1·4953	1·5032
Tl	1·4930	1·4982	1·5060
Cd	1·4946	1·4998	1·5076
F	1·4964	1·5014	1·5094
G	1·5018	1·5067	1·5148

Mean of α, β, and γ for Na light = 1·4962.

α = Vibration direction parallel to second median line, 6° 19′ in front of axis *c*.
β = ,, ,, ,, ,, symmetry axis *b*.
γ = ,, ,, ,, ,, first median line.

Murmann and Rotter found indirectly for yellow light $\alpha = 1{\cdot}489$, $\beta = 1{\cdot}494$, and $\gamma = 1{\cdot}501$; also β for red light $= 1{\cdot}492$, and for green light $= 1{\cdot}497$.

General Formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}4826 + \frac{441\,773}{\lambda^2} + \frac{449\,400\,000\,000}{\lambda^4} + \ldots$$

The index α is reproduced also by the formula if the constant 1·4826 is diminished by 0·0051, and γ if it is increased by 0·0079.

Observations at 70° showed that the refractive indices of ammonium cobalt sulphate are diminished by about 0·0020 (for α) to 0·0025 (for γ) by 55° rise of temperature.

In the next table the refractive indices of the four cobalt-containing salts are compared.

Comparison of the Refractive Indices.

Index.	Light.	KCo sulphate.	RbCo sulphate.	NH_4Co sulphate.	CsCo sulphate.
α	Li	1·4780	1·4833	1·4871	1·5028
	C	1·4784	1·4837	1·4876	1·5032
	Na	1·4807	1·4859	1·4902	1·5057
	Tl.	1·4830	1·4882	1·4930	1·5079
	F	1·4861	1·4910	1·4964	1·5112
	G	1·4904	1·4954	1·5018	1·5159
β	Li	1·4838	1·4889	1·4922	1·5057
	C	1·4842	1·4893	1·4927	1·5061
	Na	1·4865	1·4916	1·4953	1·5085
	Tl	1·4889	1·4940	1·4982	1·5110
	F	1·4919	1·4968	1·5014	1·5142
	G	1·4961	1·5011	1·5067	1·5188
γ	Li	1·4973	1·4985	1·5001	1·5102
	C	1·4977	1·4989	1·5006	1·5106
	Na	1·5004	1·5014	1·5032	1·5132
	Tl	1·5028	1·5038	1·5060	1·5156
	F	1·5059	1·5068	1·5094	1·5187
	G	1·5105	1·5114	1·5148	1·5237
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4892	1·4930	1·4962	1·5091
Double refraction, $Na_{\gamma-\alpha}$		0·0197	0·0155	0·0130	0·0075

The refractive indices of the ammonium salt, which are concisely represented by the mean index given at the foot of the table, are slightly higher than those of the rubidium salt, and the double refraction is slightly less than that of the rubidium salt, the ammonium salt thus standing between the rubidium and cæsium salts as regards both properties, and much nearer to the rubidium salt.

Axial Ratios of the Optical Ellipsoid.—These are given in the next table, both for the ammonium salt now described and for the three alkali-metal salts previously described. The comparison shows that the dimensions of the optical ellipsoid (either form) of the ammonium salt are also intermediate between those for the rubidium and cæsium salts, and much nearer to those for the rubidium salt.

AXIAL Ratios of the Optical Indicatrix.

	α	β	γ	α	β	γ
KCo sulphate . . .	0·9961	1	1·0094	0·9961	1	1·0094
RbCo ,, . . .	0·9962	1	1·0066	0·9996	1·0034	1·0100
NH_4Co ,, . . .	0·9966	1	1·0053	1·0025	1·0059	1·0113
CsCo ,, . . .	0·9981	1	1·0031	1·0129	1·0148	1·0180

AXIAL Ratios of the Optical Velocity Ellipsoid.

	$\mathfrak{a}$	$\mathfrak{b}$	$\mathfrak{c}$	$\mathfrak{a}$	$\mathfrak{b}$	$\mathfrak{c}$
KCo sulphate . . .	1·0039	1	0·9907	1·0039	1	0·9907
RbCo ,, . . .	1·0038	1	0·9935	1·0004	0·9966	0·9901
NH_4Co ,, . . .	1·0034	1	0·9947	0·9975	0·9941	0·9889
CsCo ,, . . .	1·0019	1	0·9969	0·9872	0·9854	0·9823

Molecular Optical Constants.—These are given in the next three tables for all four salts of the cobalt group. The newly determined densities were employed in recalculating the values for the three alkali-metal salts. The specific refraction and dispersion of the ammonium salt are considerably higher than those of the three salts containing the alkali metals. The molecular dispersion of the ammonium salt is slightly higher than that of the cæsium salt. The molecular refraction, either of LORENZ or GLADSTONE and DALE, is invariably just higher than that of the rubidium salt, a fact which is very clearly demonstrated by the mean molecular refraction given in the last column of the third table.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.						Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmCo . . .	0·1515	0·1528	0·1549	0·1552	0·1565	0·1586	0·0037	0·0037	0·0037
KCo. . . .	0·1277	0·1290	0·1320	0·1304	0·1317	0·1349	0·0027	0·0027	0·0029
RbCo . . .	0·1144	0·1125	0·1144	0·1137	0·1148	0·1168	0·0023	0·0023	0·0024
CsCo. . . .	0·1040	0·1045	0·1053	0·1062	0·1067	0·1075	0·0022	0·0022	0·0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d} = \mathfrak{m}$.						Molecular dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KCo sulphate	55·43	56·00	57·33	56·61	57·17	58·57	1·18	1·17	1·24
RbCo ,,	58·63	59·20	60·19	59·83	60·41	61·48	1·20	1·21	1·29
AmCo ,,	59·43	59·95	60·77	60·89	61·40	62·22	1·46	1·45	1·45
CsCo ,,	64·50	64·81	65·30	65·87	66·18	66·71	1·37	1·37	1·41

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KCo sulphate	93·61	94·75	97·35	95·24
RbCo ,, ...	99·17	100·32	102·29	100·59
AmCo ,, ...	100·64	101·70	103·33	101·89
CsCo ,, ...	109·75	110·39	111·37	110·50

Optic Axial Angle.—The results with three pairs of section-plates perpendicular to the first and second median lines are given in the two next tables. The angle in air, although very large, was just clearly visible in all three of the plates ground perpendicular to the first median line, but the absorption at the blue end of the spectrum prevented trustworthy observations being obtained beyond the wave-length of Tl light.

APPARENT Optic Axial Angle in Air, 2E, of AmCo Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ′	° ′	° ′	° ′
Li	156 1	157 34	155 16	156 17
C	156 20	157 51	155 34	156 35
Na	158 32	159 52	157 29	158 38
Tl	160 40	162 0	159 40	160 47

A determination of 2E at 70° with Plate 1 gave the value 153° 5′ for sodium light, indicating that the optic axial angle in air diminishes with rise of temperature to the extent of $5\frac{1}{2}$° for 55° of rise.

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	72 31	1*a*	85 46	81 59	82 1
	2	72 53	2*a*	85 51	82 12	
	3	72 29	3*a*	85 55	81 53	
C	1	72 30	1*a*	85 43	82 0	82 2
	2	72 51	2*a*	85 46	82 13	
	3	72 27	3*a*	85 50	81 54	
Na	1	72 18	1*a*	85 16	82 6	82 9
	2	72 43	2*a*	85 22	82 20	
	3	72 16	3*a*	85 22	82 2	
Tl	1	72 9	1*a*	84 48	82 16	82 17
	2	72 35	2*a*	84 58	82 28	
	3	72 4	3*a*	84 57	82 8	
Cd	1	72 3	1*a*	84 33	82 20	82 21
	2	72 29	2*a*	84 43	82 32	
	3	71 58	3*a*	84 42	82 12	
F	1	71 56	1*a*	84 14	82 26	82 27
	2	72 22	2*a*	84 24	82 38	
	3	71 51	3*a*	84. 23	82 17	

MURMANN and ROTTER obtained 155° 12′ for 2E, and 81° 39′ for $2V_a$ (no specific wave-length).

Dispersion of the Median Lines.—The inclined dispersion is very minute, and is such that the first median line is nearer to the axis *a* by about eight minutes for red C-hydrogen light than for green thallium light. The determinations were carried out with Plates 1, 2 and 3 immersed in toluene, the refractive index of which (1·4955) is almost identical with the mean refraction (1·4962) of ammonium cobalt sulphate.

OPTIC Axial Angles $2V_a$ of the Cobalt Group.

	KCo sulphate.	RbCo sulphate.	CsCo sulphate.	AmCo sulphate.
	° ′	° ′	° ′	° ′
Li	68 38	75 15	81 42	82 1
C	68 39	75 14	81 40	82 2
Na	68 41	75 11	81 34	82 9
Tl	68 44	75 8	81 29	82 17
F	68 48	75 3	81 22	82 27

The last table comparing the optic axial angles of the four cobalt-containing salts shows that the angle of the ammonium salt is just slightly greater than that of the cæsium salt. All four salts are positive.

Ammonium Manganese Sulphate, $(NH_4)_2\,Mn(SO_4)_2 \cdot 6H_2O$.

Morphology.

Crystals of this salt were measured by MURMANN and ROTTER (*loc. cit.*, p. 148), and also to some extent by GRAILICH[*] and by SCACCHI[†]. The results of MURMANN and ROTTER are given in the next to the last column of the table of angles, and those of GRAILICH (G) and of SCACCHI (S) in the last column.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—$a : b : c = 0·7400 : 1 : 0·4931$. Values of MURMANN and ROTTER, 0·7359 : 1 : 0·4972.

Axial Angle.—$\beta = 106° \, 51'$. Value of MURMANN and ROTTER, 107° 2′.

Forms observed.—$a\,\{100\}$, $b\,\{010\}$, $c\,\{001\}$, $p\,\{110\}$, $p'\{120\}$, $p'''\{130\}$, $q\,\{011\}$, $r'\,\{\bar{2}10\}$, $o\,\{111\}$, $o'\,\{\bar{1}11\}$. MURMANN and ROTTER also found a minute face of $n'\,\{\bar{1}21\}$ on one crystal.

Habit.—Prismatic (primary prism $p\,\{110\}$) parallel axis c. The prisms are sometimes fairly long, but more frequently short.

Ten good crystals were measured, obtained from five different crops. The results are given in the table of angles. The crystals were beautifully transparent in the crops retained for use, but some other crops showed an appreciable amount of turbidity. They are not quite colourless, a faint pink tint appearing to be an essential property of the salt which in the cases of truly transparent crystals renders them very beautiful, especially when a number are seen together against a white background. Great care is required in growing them for goniometrical purposes, as crops grown without the precautions indicated in the author's "Crystallography and Practical Crystal Measurement" (p. 9) show more facial irregularities than many other salts of this series.

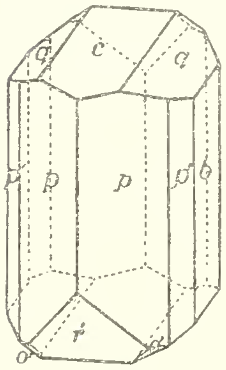

Fig. 6.

The primary prism $p\,\{110\}$ is generally the largely predominating form, closely followed by the basal plane $c\,\{001\}$, as shown in fig. 1. Often, however, the latter form c is less prominent, the faces of $q\,\{011\}$ being relatively larger and the orthopinakoid $r'\,\{\bar{2}01\}$ being exceptionally well developed, as shown in fig. 6. Occasionally crystals were also seen, and one was measured, having large $b\,\{010\}$ faces. The hemipyramid faces $o'\,\{\bar{1}11\}$ (common) and $o\,\{111\}$ (rarer) were usually somewhat distorted, rarely giving images of the signal so good as those derived from the faces of other forms. The prismatic form $p'\{120\}$ was fairly common, appearing as a strip, but the prism $p'''\{130\}$ was much more rarely developed. The orthopinakoid $a\,\{100\}$ was only once seen, and was then merely a fine narrow strip affording an image too faint for absolute measurement. The face $n'\{\bar{1}21\}$ recorded by MURMANN

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[*] 'Krystallogr.-optische Untersuchungen, Preisschr. Wien,' 1858, 140.

[†] 'Il Giambattista-Vico, Giornale Scientifico,' Naples, 1857, fasc. 6, sep. 9.

Interfacial Angles of Ammonium Manganese Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of M. & R.	Values of G. & S.
		′ ′	′	′	′	° ′	° ′
ac = $(100):(001)$	—	—	—	73 9	—	72 58	71 42 G.
as = $(100):(101)$	—	—	—	45 1	—	—	—
sc = $(101):(001)$	—	—	—	28 8	—	—	—
cr′ = $(001):(\bar{2}01)$	10	64 7– 64 25	64 15	64 19	4	64 18	—
cs′ = $(001):(\bar{1}01)$	—	—	—	38 20	—	—	—
s′r′ = $(\bar{1}01):(\bar{2}01)$	—	—	—	25 59	—	—	—
r′a = $(\bar{2}01):(\bar{1}00)$	—	—	—	42 32	—	42 6	—
r′c = $(\bar{2}01):(00\bar{1})$	10	115 33–116 0	115 45	115 41	4	—	—
ap = $(100):(110)$	—	—	—	35 18	—	35 40	—
pp′ = $(110):(120)$	8	19 17– 19 33	19 27	19 28	1	19 17	—
p′b = $(120):(010)$	2	35 8– 35 22	35 15	35 14	1	35 25	—
pp‴ = $(110):(130)$	—	—	—	29 29	—	—	—
p‴b = $(130):(010)$	1	—	25 19	25 13	6	25 45	—
pb = $(110):(010)$	40	54 36– 54 55	54 42	*	—	54 57	—
pp = $(110):(1\bar{1}0)$	21	70 22– 70 47	70 35	70 36	1	70 16	70 35 G. 70 32 S.
cq = $(001):(011)$	29	25 4– 25 33	25 16	*	—	24 35	24 55 G. 25 13 S.
qb = $(011):(010)$	18	64 31– 64 48	64 44	64 44	0	—	—
ao = $(100):(111)$	—	—	—	48 8	—	—	—
oq = $(111):(011)$	—	—	—	26 40	—	—	—
aq = $(100):(011)$	—	—	—	74 48	—	—	—
qo′ = $(011):(\bar{1}11)$	1	—	34 34	34 38	4	—	—
o′a = $(\bar{1}11):(\bar{1}00)$	—	—	—	70 34	—	—	—
co = $(001):(111)$	1	—	33 41	33 38	3	—	—
op = $(111):(110)$	1	—	42 40	42 41	1	—	—
cp = $(001):(110)$	40	76 13– 76 30	76 19	*	—	—	76 24 S.
po′ = $(110):(11\bar{1})$	21	58 49– 59 24	59 4	59 10	6	—	—
o′c = $(11\bar{1}):(00\bar{1})$	20	44 27– 44 52	44 38	44 31	7	—	—
bn = $(010):(121)$	—	—	—	55 6	—	—	—
no = $(121):(111)$	—	—	—	15 40	—	—	—
bo = $(010):(111)$	—	—	—	70 46	—	—	—
os = $(111):(101)$	—	—	—	19 14	—	—	—
bo′ = $(010):(\bar{1}11)$	1	—	65 16	65 21	5	—	—
o′s′ = $(\bar{1}11):(\bar{1}01)$	—	—	—	24 39	—	—	—
o′o′ = $(\bar{1}11):(\bar{1}\bar{1}1)$	1	—	49 25	49 18	7	—	—
sq = $(101):(011)$	—	—	—	37 6	—	—	—
qp = $(011):(\bar{1}10)$	24	87 57– 88 28	88 9	88 8	1	—	—
ps = $(\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 46	—	—	—
pq = $(\bar{1}10):(0\bar{1}\bar{1})$	24	91 40– 92 4	91 50	91 52	2	—	—
s′q = $(\bar{1}01):(011)$	—	—	—	44 49	—	—	—
qn = $(011):(121)$	—	—	—	26 3	—	—	—
np = $(121):(110)$	—	—	—	36 31	—	—	—
qp = $(011):(110)$	25	62 24– 62 42	62 33	62 34	1	—	—
ps′ = $(110):(10\bar{1})$	—	—	—	72 37	—	—	—
pq = $(110):(0\bar{1}\bar{1})$	24	117 23–117 41	117 28	117 26	2	—	—
r′o′ = $(\bar{2}01):(\bar{1}11)$	11	34 51– 35 24	35 7	35 13	6	35 25	—
o′p = $(\bar{1}11):(110)$	16	91 34– 92 5	91 50	91 45	5	91 47	—
pr′ = $(110):(20\bar{1})$	24	52 52– 53 26	53 6	53 2	4	52 22	—
Total number of measurements .	373						

and ROTTER was never seen on this salt, although the author has observed it on other salts of the series.

In the next three tables the morphological constants of the three salts containing manganese are compared. From the first table it will be observed that the axial angle β of the ammonium salt is fairly near to that of the cæsium salt, and that the axial ratios of the ammonium and rubidium salts are also close to each other; the values for the ammonium salt clearly indicate the propriety of including this salt in this isomorphous series of double salts.

The impossibility of preparing potassium manganese sulphate renders as complete a comparison as usual of the interfacial angles of a group impossible; but the angles of the ammonium salt are very obviously related to those of the rubidium and cæsium salts in a manner similar to that which has been observed in the other groups investigated, where the complete set of four salts has been obtained. Like the axial ratios, the angles indicate clearly that the ammonium salt does belong to the same series as the rubidium and cæsium salts.

Cleavage.—There is an excellent cleavage parallel to the orthopinakoid $r'\{\bar{2}01\}$, and also a fairly good cleavage parallel to the clinopinakoid $b\ \{010\}$.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Rubidium manganese sulphate .	105° 57′	0·7382 : 1 : 0·4950
Ammonium ,, ,, .	106° 51′	0·7400 : 1 : 0·4931
Cæsium ,, ,, .	107° 7′	0·7274 : 1 : 0·4913

COMPARISON of the Interfacial Angles.

Angle.	RbMn sulphate.	CsMn sulphate.	AmMn sulphate.
	° ′	° ′	° ′
ac = (100) : (001)	74 3	72 53	73 9
as = (100) : (101)	45 27	44 37	45 1
sc = (101) : (001)	28 36	28 16	28 8
cr' = (001) : ($\bar{2}$01)	63 58	64 55	64 19
cs' = (001) : ($\bar{1}$01)	38 23	38 48	38 20
$s'r'$ = ($\bar{1}$01) : ($\bar{2}$01)	25 35	26 7	25 59
$r'a$ = ($\bar{2}$01) : ($\bar{1}$00)	41 59	42 12	42 32
ap = (100) : (110)	35 20	34 51	35 18
pp' = (110) : (120)	19 28	19 28	19 28
$p'b$ = (120) : (010)	35 12	35 41	35 14
pb = (110) : (010)	54 40	55 9	54 42
cq = (001) : (011)	25 30	25 11	25 16
qb = (011) : (010)	64 30	64 49	64 44

COMPARISON of the Interfacial Angles (continued).

Angle.	RbMn sulphate.	CsMn sulphate.	AmMn sulphate.
	° ′	° ′	° ′
ao = $(100) : (111)$	48 34	47 43	48 8
oq = $(111) : (011)$	27 4	26 50	26 40
aq = $(100) : (011)$	75 38	74 33	74 48
qo′ = $(011) : (\bar{1}11)$	34 40	35 5	34 38
o′a = $(\bar{1}11) : (\bar{1}00)$	69 42	70 22	70 34
co = $(001) : (111)$	34 6	33 38	33 38
op = $(111) : (110)$	42 57	42 23	42 41
cp = $(001) : (110)$	77 3	76 1	76 19
po′ = $(110) : (11\bar{1})$	58 25	59 8	59 10
o′c = $(11\bar{1}) : (00\bar{1})$	44 32	44 51	44 31
bo = $(010) : (111)$	70 34	70 58	70 46
os = $(111) : (101)$	19 26	19 2	19 14
bo′ = $(010) : (\bar{1}11)$	65 25	65 27	65 21
o′s′ = $(\bar{1}11) : (\bar{1}01)$	24 35	24 33	24 39
sq = $(101) : (011)$	37 35	37 9	37 6
qp = $(011) : (\bar{1}10)$	87 20	88 36	88 8
ps = $(\bar{1}10) : (\bar{1}0\bar{1})$	55 5	54 15	54 46
s′q = $(\bar{1}01) : (011)$	44 58	45 9	44 49
qp = $(01\bar{1}) : (110)$	63 10	62 30	62 34
ps′ = $(110) : (10\bar{1})$	71 52	72 21	72 37
r′o′ = $(\bar{2}01) : (\bar{1}11)$	34 54	35 14	35 13
o′p = $(\bar{1}11) : (110)$	92 26	92 13	91 45
pr′ = $(\bar{1}10) : (20\bar{1})$	52 40	52 33	53 2

Volume.

Relative Density.—Five determinations by the immersion method yielded the following results :—

I.	Density for 16°·2/4°	1·8324	For 20°/4°		1·8317
II.	,, 15°·7/4°	1·8300	,, 20°/4°		1·8292
III.	,, 16°·1/4°	1·8319	,, 20°/4°		1·8312
IV.	,, 17°·6/4°	1·8312	,, 20°/4°		1·8308
V.	,, 17°·3/4°	1·8329	,, 20°/4°		1·8324
				Mean	1·8311

Accepted value for 20°/4°, **1·831**.

A determination by SCHROEDER* gave the density 1·825.

Molecular Volume.—$\frac{M}{d} = \frac{388{\cdot}42}{1{\cdot}831} = 212{\cdot}13.$

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* 'Journ. für Prakt. Chemie,' 1879, [2], 19, 266.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6·2670 : 8·4690 : 4·1761.$$

Redeterminations of Densities of Rubidium and Cæsium Manganese Sulphates.

Rubidium Manganese Sulphate, $Rb_2Mn(SO_4)_2 . 6H_2O$.

I.	Density for 14°·9/4° . . .	2·4617	For 20°/4° . . .	2·4605
II.	,, 16°·5/4° . . .	2·4613	,, 20°/4° . . .	2·4604
III.	,, 16°·1/4° . . .	2·4607	,, 20°/4° . . .	2·4597
IV.	,, 16°·6/4° . . .	2·4622	,, 20°/4° . . .	2·4614
			Mean . . .	2·4605

Accepted value for 20°/4°, **2·461**. Former pyknometer value 2·459.

Cæsium Manganese Sulphate, $Cs_2Mn(SO_4)_2 . 6H_2O$.

I.	Density for 18°·9/4° . . .	2·7397	For 20°/4° . . .	2·7394
II.	,, 19°·3/4° . . .	2·7420	,, 20°/4° . . .	2·7418
III.	,, 19°·7/4° . . .	2·7409	,, 20°/4° . . .	2·7408
IV.	,, 17°·2/4° . . .	2·7373	,, 20°/4° . . .	2·7365
			Mean . . .	2·7396

Accepted value for 20°/4°, **2·740**. Former pyknometer value 2·738.

The next table affords a comparison of the volume constants of the three salts, employing the new densities.

VOLUME Constants of the Manganese Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios. $\chi : \psi : \omega$
RbMn sulphate . .	522·36	2·461	212·26	6·2404 : 8·4536 : 4·1846
NH_4Mn ,, . .	388·42	1·831	212·13	6·2670 : 8·4690 : 4·1761
CsMn ,, . .	616·36	2·740	224·95	6·3286 : 8·7004 : 4·2745

From this table it will be apparent that the molecular volume and topic axial ratios of ammonium manganese sulphate are very close to the values of these constants for the rubidium salt. The molecular volume and the ratio ω are very slightly lower, and the ratios χ and ψ slightly higher.

Optics.

Orientation of the Optical Ellipsoid.—The symmetry plane $b\ \{010\}$ is the plane of the optic axes, and the sign of double refraction is positive. The first median line is the axis γ of the optical indicatrix, and the second median line corresponds to the α refractive index.

A pair of section-plates parallel to the symmetry plane afforded the following angles for the extinction direction corresponding to the second median line :—

Inclination of 2M.L. *from normal to c* {001}.

Plate 1 . . .	9° 24′	Plate 2 . . .	9° 6′
	Mean . . .	9° 15′	

The direction is behind the normal. As the axial angle *ac* = 73° 9′ this extinction direction is 7° 36′ in front of the vertical axis *c*, and the first median line extinction is 9° 15′ above the axis *a*, both axes of the optical indicatrix which lie in the symmetry plane being thus in the obtuse angle of the morphological axes *ac*. MURMANN and ROTTER found the two extinctions 8° 36′ in front of *c*, and 8° 26′ above *a*. In the next table the positions of the optical indicatrix of the three manganese salts are compared, and in fig. 7 they are graphically illustrated.

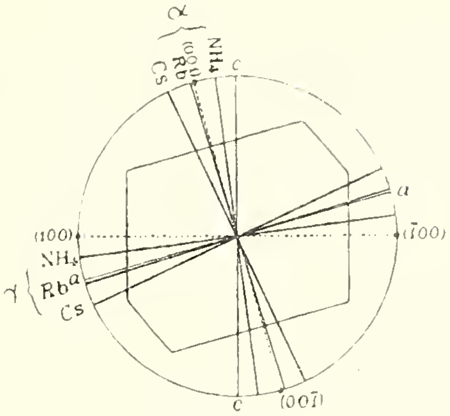

Fig. 7.

Inclinations of α Axis of Indicatrix (2M.L.) *of the Manganese Salts in front of Axis c.*

AmMn sulphate		7° 36′
RbMn	,,	16° 57′
CsMn	,,	25° 27′

Although the potassium salt is missing, the relations of the indicatrices of the ammonium, rubidium, and cæsium manganese salts are similar to what has been observed in groups which are complete, the ammonium salt indicatrix standing with its α-axis nearest to the vertical axis of the crystal *c*.

Refractive Indices.—The results with six prisms, each ground so as to afford directly two indices, are given in the accompanying table.

REFRACTIVE Indices of Ammonium Manganese Sulphate.

Light.	α.	β.	γ.
Li	1·4770	1·4810	1·4882
C	1·4775	1·4815	1·4887
Na	1·4801	1·4840	1·4913
Tl	1·4827	1·4865	1·4940
Cd	1·4842	1·4881	1·4956
F.	1·4858	1·4897	1·4971
G.	1·4912	1·4951	1·5025

Mean of α, β, and γ for Na light = 1·4851.

α = Vibration direction parallel to second median line, 7° 36′ in front of axis *c*.
β = ,, ,, ,, ,, symmetry axis *b*.
γ = ,, ,, ,, ,, first median line.

Murmann and Rotter obtained for β in red light 1·482, in yellow light 1·484, and in green light 1·485.

General Formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}4691 + \frac{633\,924}{\lambda^2} - \frac{3\,568\,840\,000\,000}{\lambda^4} + \ldots .$$

The index α is also reproduced by the formula if the constant 1·4691 is diminished by 0·0039, and the γ index if the constant is increased by 0·0073.

Observations at 70° showed that the refractive indices of ammonium manganese sulphate diminish by about 0·0019 (for α) to 0·0021 (for γ) for 55° rise of temperature.

In the next table the refractive indices of the three salts containing manganese are compared.

Comparison of the Refractive Indices.

Index.	Light.	RbMn sulphate.	NH_4Mn sulphate.	CsMn sulphate.
α	Li	1·4741	1·4770	1·4918
	C	1·4745	1·4775	1·4922
	Na	1·4767	1·4801	1·4946
	Tl	1·4791	1·4827	1·4972
	F	1·4821	1·4858	1·5003
	G	1·4864	1·4912	1·5046
β	Li	1·4781	1·4810	1·4936
	C	1·4785	1·4815	1·4940
	Na	1·4807	1·4840	1·4966
	Tl	1·4831	1·4865	1·4991
	F	1·4860	1·4897	1·5022
	G	1·4907	1·4951	1·5066
γ	Li	1·4880	1·4882	1·4995
	C	1·4884	1·4887	1·4999
	Na	1·4907	1·4913	1·5025
	Tl	1·4933	1·4940	1·5051
	F	1·4965	1·4971	1·5083
	G	1·5015	1·5025	1·5129
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4827	1·4851	1·4979
Double refraction, $Na_{\gamma-\alpha}$		0·0140	0·0112	0·0079

The position of the ammonium salt as regards refractive indices is precisely similar to that in the nickel and cobalt groups already dealt with, namely, just beyond that of the rubidium salt, the indices of which are only very slightly lower. The ammonium salt also occupies an intermediate position between the rubidium and cæsium salts as regards double refraction, the value being slightly nearer to that of the rubidium salt.

Axial Ratios of the Optical Ellipsoid.—These are given in the next table, and compared with the corresponding values for rubidium and cæsium manganese sulphates.

	Axial Ratios of Optical Indicatrix.	Axial Ratios of Optical Velocity Ellipsoid.
	$\alpha : \beta : \gamma$	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$
RbMn sulphate . . .	0·9973 : 1 : 1·0067	1·0027 : 1 : 0·9933
NH_4Mn ,, . . .	0·9974 : 1 : 1·0049	1·0026 : 1 : 0·9951
CsMn ,, . . .	0·9987 : 1 : 1·0039	1·0013 : 1 : 0·9961

The values when β for the same salt $= 1$ show a similar arrangement as in the groups previously described, with the ammonium salt intermediate between the rubidium and cæsium salts. The potassium salt not existing, the values cannot be calculated on the basis of $\beta_{\text{K salt}} = 1$.

Molecular Optical Constants.—These are given in the following three tables, and compared with the analogous values for the rubidium and cæsium salts, using the newly determined values of the densities of the latter salts in the calculations for these salts. The specific refraction and dispersion of the ammonium salt again stand out prominently higher than those of the alkali-metal salts, and the molecular dispersion of ammonium manganese sulphate is slightly higher than that of the cæsium salt. The molecular refraction, calculated by either formula, of the ammonium salt is just slightly higher than that of the rubidium salt, the relationship being very concisely expressed by the mean molecular refraction shown at the conclusion of the third table.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.						Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C ($H\alpha$).			For ray $H\gamma$ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmMn . . .	0·1545	0·1556	0·1576	0·1582	0·1593	0·1613	0·0037	0·0037	0·0037
RbMn . . .	0·1143	0·1151	0·1172	0·1167	0·1176	0·1198	0·0024	0·0025	0·0026
CsMn . . .	0·1059	0·1062	0·1073	0·1082	0·1085	0·1097	0·0023	0·0023	0·0024

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$.						Molecular dispersion, $m_G - m_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
RbMn sulphate	59·70	60·13	61·19	60·98	61·44	62·59	1·28	1·31	1·40
AmMn ,,	59·99	60·42	61·20	61·46	61·87	62·66	1·47	1·45	1·46
CsMn ,,	65·29	65·48	66·15	66·67	66·90	67·60	1·38	1·42	1·45

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
RbMn sulphate	100·72	101·56	103·65	101·98
AmMn ,, ...	101·29	102·14	103·67	102·37
CsMn ,, ...	110·72	111·12	112·45	111·43

Optic Axial Angle.—The determinations with three pairs of excellent section-plates are given in the two following tables.

APPARENT Optic Axial Angle in Air, 2E, of AmMn Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ′	° ′	° ′	° ′
Li	115 46	115 22	114 57	115 22
C	115 58	115 31	115 6	115 32
Na	116 51	116 8	116 9	116 23
Tl	117 18	116 53	116 50	117 0
Cd	117 43	117 2	116 59	117 15
F	118 5	117 25	117 10	117 33

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	61 34	1*a*	94 26	69 47	69 45
	2	61 34	2*a*	94 29	69 45	
	3	61 29	3*a*	94 24	69 44	
C	1	61 31	1*a*	94 21	69 47	69 46
	2	61 32	2*a*	94 25	69 46	
	3	61 28	3*a*	94 20	69 45	
Na	1	61 18	1*a*	93 52	69 48	69 49
	2	61 22	2*a*	94 0	69 48	
	3	61 21	3*a*	93 53	69 51	
Tl	1	61 9	1*a*	93 27	69 53	69 54
	2	61 13	2*a*	93 25	69 57	
	3	61 8	3*a*	93 26	69 53	
Cd	1	61 0	1*a*	92 58	69 58	70 0
	2	61 5	2*a*	92 59	70 2	
	3	61 3	3*a*	92 58	70 1	
F	1	60 50	1*a*	92 38	70 0	70 2
	2	60 54	2*a*	92 38	70 3	
	3	60 54	3*a*	92 37	70 3	

MURMANN and ROTTER obtained for 2E 114° 45′, and for $2V_a$ 69° 9′ (no wave-length specified).

A determination of 2E at 70° with Plate 2 showed that the optic axial angle in air diminishes by about 4° for 55° rise of temperature.

Dispersion of the Median Lines.—The inclined dispersion is again small in ammonium manganese sulphate, the first median line lying nearer by 10′ only to the axis *a* for red lithium light than for greenish-blue F light. The determination was carried out by immersion of the Plates 1, 2, and 3 in toluene.

The optic axial angle of ammonium manganese sulphate is shown in the following comparative table to be slightly larger than that of the rubidium salt.

OPTIC Axial Angles $2V_a$ of the Manganese Group.

	AmMn sulphate.	RbMn sulphate.	CsMn sulphate.
	° ′	° ′	° ′
Li	69 45	67 10	60 10
C	69 46	67 8	60 7
Na	69 49	67 5	59 57
Tl	69 54	67 1	59 46
F	70 2	66 55	59 28

Ammonium Copper Sulphate, $(NH_4)_2 Cu (SO_4)_2 . 6H_2O$.

Morphology.

Crystals of this salt were measured in the year 1835 by MILLER,[*] who observed the forms *a*, *c*, *p*, *q*, *r'*, and *o'*, of those enumerated in the list of forms given below. MURMANN and ROTTER included the salt in their optical investigation of 1859 (*loc. cit.*, p. 170), and observed the further forms *b* and *p'*; but they did not record any accurate measurements of the crystal angles. MILLER'S values are quoted in the last column of the table of angles now given.

Crystal System.—Monoclinic Class No. 5, holohedral-prismatic.

Ratios of Axes.—

$a : b : c = 0·7463 : 1 : 0·5066$. Values of MILLER, $0·7433 : 1 : 0·4838$.

Axial Angle.—$\beta = 106° 9'$. Value of MILLER, $106° 6'$.

Forms observed.—*a* {100}, *b* {010}, *c* {001}, *p* {110}, *p'*{120}, *p'''*{130}, *q* {011}, *r'*{$\bar{2}$01}, *o* {111}, *o'*{$\bar{1}$11}.

Habit.—Short prismatic parallel to *p* {110}, or tabular parallel to *c* {001}.

Eleven perfectly transparent crystals were measured of this beautiful pale blue salt, selected from seven different crops. They were of the two types shown in figs. 8 and 9, and of intermediate types.

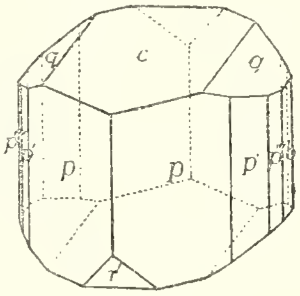

Fig. 8.

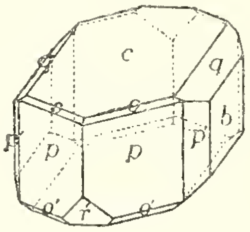

Fig. 9.

Many crystals of the numerous crops prepared were very simple, exhibiting only the forms *c* {001}, *p* {110}, *q* {011}, and *r'*{$\bar{2}$01}. On numerous others small or narrow representatives of the other forms mentioned in the list of forms were present. On a good number of the crystals of the crops from which individuals were selected for measurement there were well developed faces of the clinopinakoid *b* {010}, the rarer prisms *p'*{120} and *p'''*{130}, and the hemipyramids *o* {111} and *o'*{$\bar{1}$11}. Traces only of the orthopinakoid *a* {100} were observed, no measurements being possible. The variation of the length of the faces of the prism zone causes the variation of habit from prismatic along *p* {110} to tabular parallel to *c* {001}. Both these forms showed striation in many of the crops prepared, but the crops used were composed of crystals exhibiting this property at a minimum, and several of the measured crystals were quite free from striation. The face in contact with the bottom of the crystallising vessel had been either *p* or *c*.

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[*] 'Phil. Mag.' 1835, [3], 6, 105; 'Pogg. Ann. der Phy., 1835, 36, 477.

INTERFACIAL Angles of Ammonium Copper Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of MILLER.
		° ′ ° ′	° ′	° ′	′	° ′
$ac = (100):(001)$	—	—	—	73 51	—	73 54
$as = (100):(101)$	—	—	—	45 5	—	—
$sc = (101):(001)$	—	—	—	28 46	—	—
$cr' = (001):(\bar{2}01)$	6	64 37– 64 42	64 38	64 33	5	64 54
$cs' = (001):(\bar{1}01)$	—	—	—	38 51	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 42	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	—	—	—	41 36	—	—
$r'c = (\bar{2}01):(00\bar{1})$	3	115 17–115 23	115 22	115 27	5	—
$ap = (100):(110)$	—	—	—	35 38	—	—
$pp' = (110):(120)$	3	19 26– 19 26	19 26	19 28	2	—
$p'b = (120):(010)$	2	34 42– 35 1	34 52	34 54	2	—
$p'p''' = (120):(130)$	1	—	9 53	9 58	5	—
$pp''' = (110):(130)$	1	—	29 24	29 26	2	—
$p'''b = (130):(010)$	1	—	24 58	24 56	2	—
$pb = (110):(010)$	24	54 8– 54 37	54 22	*	—	—
$pp = (110):(1\bar{1}0)$	19	71 4– 71 27	71 16	71 16	0	71 4
$cq = (001):(011)$	29	25 34– 26 16	25 57	*	—	26 10
$qb = (011):(010)$	29	63 40– 64 27	64 3	64 3	0	—
$ao = (100):(111)$	—	—	—	48 21	—	—
$oq = (111):(011)$	1	—	27 8	27 10	2	—
$aq = (100):(011)$	—	—	—	75 31	—	—
$qo' = (011):(\bar{1}11)$	1	—	34 59	34 54	5	—
$o'a = (\bar{1}11):(\bar{1}00)$	—	—	—	69 35	—	69 11
$co = (001):(111)$	4	34 12– 34 32	34 26	34 24	2	—
$op = (111):(110)$	5	42 21– 42 29	42 27	42 32	5	—
$cp = (001):(110)$	40	76 41– 77 12	76 56	*	—	—
$po' = (110):(11\bar{1})$	1	—	57 52	57 59	7	—
$o'c = (11\bar{1}):(00\bar{1})$	1	—	45 12	45 5	7	45 31
$bn = (010):(121)$	—	—	—	54 21	—	—
$no = (121):(111)$	—	—	—	15 55	—	—
$bo = (010):(111)$	1	—	70 17	70 16	1	—
$os = (111):(101)$	—	—	—	19 44	—	—
$bo' = (010):(\bar{1}11)$	1	—	64 57	64 57	0	—
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	25 3	—	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	—	—	—	50 6	—	—
$sq = (101):(011)$	—	—	—	37 59	—	—
$qp = (011):(\bar{1}10)$	17	86 38– 87 23	87 4	87 2	2	—
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 59	—	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	16	92 40– 93 7	92 56	92 58	2	—
$s'q = (\bar{1}01):(011)$	—	—	—	45 33	—	—
$qn = (011):(121)$	—	—	—	26 26	—	—
$np = (121):(110)$	—	—	—	36 18	—	—
$qp = (011):(110)$	21	62 32– 62 57	62 44	62 44	0	—
$ps' = (110):(10\bar{1})$	—	—	—	71 43	—	—
$pq = (110):(0\bar{1}\bar{1})$	20	117 0–117 32	117 16	117 16	0	—
$r'o' = (\bar{2}01):(\bar{1}11)$	1	—	35 12	35 16	4	—
$o'p = (\bar{1}11):(110)$	1	—	92 16	92 9	7	—
$pr' = (110):(20\bar{1})$	7	52 23– 52 42	52 31	52 35	4	—
Total number of measurements . .	256					

In the three following tables the morphological constants of the four salts containing copper are compared. The first shows that the axial angles of the ammonium and cæsium copper salts are almost identical, and that the axial ratios are such as place the ammonium salt indubitably in the same isomorphous series with the alkali-metal salts.

COMPARISON of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium copper sulphate . .	104° 28′	0·7490 : 1 : 0·5088
Rubidium ,, ,, . .	105° 18′	0·7490 : 1 : 0·5029
Ammonium ,, ,, . .	106° 9′	0·7463 : 1 : 0·5066
Cæsium ,, ,, . .	106° 10′	0·7429 : 1 : 0·4946

COMPARISON of the Interfacial Angles.

Angle.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.	AmCu sulphate.
	° ′	° ′	° ′	° ′
$ac = (100):(001)$	75 32	74 42	73 50	73 51
$as = (100):(101)$	46 11	45 53	45 29	45 5
$sc = (101):(001)$	29 21	28 49	28 21	28 46
$cr' = (001):(\bar{2}01)$	63 19	63 30	63 50	64 33
$cs' = (001):(\bar{1}01)$	38 22	38 12	38 9	38 51
$s'r' = (\bar{1}01):(\bar{2}01)$	24 57	25 18	25 41	25 42
$r'a = (\bar{2}01):(\bar{1}00)$	41 9	41 48	42 20	41 36
$ap = (100):(110)$	35 59	35 52	35 30	35 38
$pp' = (110):(120)$	19 28	19 28	19 28	19 28
$p'b = (120):(010)$	34 33	34 40	35 2	34 54
$p'p''' = (120):(130)$	9 54	9 55	9 59	9 58
$p'''b = (130):(010)$	24 39	24 45	25 3	24 56
$pb = (110):(010)$	54 1	54 8	54 30	54 22
$cq = (001):(011)$	26 11	25 54	25 24	25 57
$qb = (011):(010)$	63 49	64 6	64 36	64 3
$ao = (100):(111)$	49 28	49 5	48 36	48 21
$oq = (111):(011)$	27 35	27 11	26 50	27 10
$aq = (100):(011)$	77 3	76 16	75 26	75 31
$qo' = (011):(\bar{1}11)$	34 30	34 24	34 28	34 54
$o'a = (\bar{1}11):(\bar{1}00)$	68 27	69 20	70 6	69 35
$co = (001):(111)$	35 6	34 31	33 55	34 24
$op = (111):(110)$	43 14	43 8	42 59	42 32
$cp = (001):(110)$	78 20	77 39	76 54	76 56
$po' = (110):(11\bar{1})$	56 58	57 50	58 44	57 59
$o'c = (11\bar{1}):(00\bar{1})$	44 42	44 31	44 22	45 5

Comparison of the Interfacial Angles (continued).

Angle.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.	AmCu sulphate.
	° ′	° ′	° ′	° ′
$bo = (010):(111)$	69 50	70 8	70 34	70 16
$os = (111):(101)$	20 10	19 52	19 26	19 44
$bo' = (010):(\bar{1}11)$	65 3	65 8	65 22	64 57
$o's' = (\bar{1}11):(\bar{1}01)$	24 57	24 52	24 38	25 3
$sq = (101):(011)$	38 32	37 59	37 21	37 59
$qp = (011):(\bar{1}10)$	85 32	86 22	87 27	87 2
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	55 56	55 39	55 12	54 59
$s'q = (\bar{1}01):(011)$	45 17	45 1	44 44	45 33
$qp = (011):(110)$	63 51	63 22	63 0	62 44
$ps' = (110):(10\bar{1})$	70 52	71 37	72 16	71 43
$r'o' = (\bar{2}01):(\bar{1}11)$	34 43	34 53	35 1	35 16
$o'p = (\bar{1}11):(110)$	92 49	92 17	91 59	92 9
$pr' = (110):(20\bar{1})$	52 28	52 50	53 0	52 35

Of the 38 angles compared in the second table, 32 show a change of angle, on passing from the potassium salt to the ammonium salt, in the same direction as is observed when rubidium or cæsium replaces potassium. Of these 32 cases, 27 show larger changes than for the rubidium replacement, and 10 even larger ones than for the cæsium replacement.

Double Sulphates containing Copper.

Replacement.	Average change.	Maximum change.
	′	′ ° ′
K by Rb	22	53
K by Cs	47	115 = 1 55
K by NH_4	39	101 = 1 41

The third small table shows that the average and maximum change of angle for the ammonium replacement is nearly as much as for the cæsium replacement, both being twice as much approximately as for the replacement of potassium by rubidium.

Cleavage.—The cleavage common to the series, parallel to $r'\{\bar{2}01\}$, is developed, but is not very facile. There is quite a good cleavage parallel to $b\ \{010\}$, and in this salt this cleavage is undoubtedly the better one of the two. The fact was confirmed on several crystals of different crops, and excellent images of the signal were obtained from the cleaved surfaces, at exactly 90 degrees from *c* faces subsisting on the fragments

Volume.

Relative Density.—Four determinations by the immersion method yielded the following values :—

I.	Density for 13°·8/4°	1·9267	For 20°/4°	1·9255
II.	,, 13°·3/4°	1·9268	,, 20°/4°	1·9255
III.	,, 13°·6/4°	1·9273	,, 20°/4°	1·9261
IV.	,, 13°·6/4°	1·9270	,, 20°/4°	1·9258
			Mean	1·9257

Accepted value for 20°/4°, **1·926**. This appears to be the first determination of the specific gravity of ammonium copper sulphate.

Molecular Volume.— $\frac{M}{d} = \frac{396\cdot92}{1\cdot926} = 206\cdot08.$

Molecular Distance Ratios (*topic axial ratios*).—

$$\chi : \psi : \omega = 6\cdot1786 : 8\cdot2790 : 4\cdot1942.$$

Redeterminations of Densities of Alkali-metal Copper Sulphates.

Potassium Copper Sulphate, $K_2Cu(SO_4)_2 . 6H_2O$.

The crystals for this determination were freshly prepared for the purpose, as this salt is the most difficult of all the potassium salts of the series to obtain in crystals free from turbidity and efflorescence. The crystals employed were almost perfectly clear, and were used immediately after removal from the mother liquor.

I.	Density for 14°·5/4°	2·2336	For 20°/4°	2·2324
II.	,, 15°·5/4°	2·2335	,, 20°/4°	2·2325
III.	,, 15°·8/4°	2·2329	,, 20°/4°	2·2320
IV.	,, 15°·9/4°	2·2351	,, 20°/4°	2·2342
			Mean	2·2328

Accepted value for 20°/4°, **2·233**.

Rubidium Copper Sulphate, $Rb_2Cu(SO_4)_2 . 6H_2O$.

I.	Density for 16°·7/4°	2·5761	For 20°/4°	2·5753
II.	,, 16°·8/4°	2·5752	,, 20°/4°	2·5744
III.	,, 16°·1/4°	2·5751	,, 20°/4°	2·5741
IV.	,, 16°·2/4°	2·5726	,, 20°/4°	2·5716
			Mean	2·5739

Accepted value for 20°/4°, **2·574**.

Cæsium Copper Sulphate, $Cs_2Cu(SO_4)_2 . 6H_2O$.

I.	Density for $19^{\circ}\cdot8/4^{\circ}$ . . .	2·8605	For $20^{\circ}/4^{\circ}$ . . .	2·8604
II.	,, $17^{\circ}\cdot2/4^{\circ}$ . . .	2·8570	,, $20^{\circ}/4^{\circ}$ . . .	2·8562
III.	,, $17^{\circ}\cdot2/4^{\circ}$ . . .	2·8591	,, $20^{\circ}/4^{\circ}$ . . .	2·8583
IV.	,, $17^{\circ}\cdot3/4^{\circ}$ . . .	2·8586	,, $20^{\circ}/4^{\circ}$ . . .	2·8578
			Mean . . .	2·8582

Accepted value for $20^{\circ}/4^{\circ}$, 2·858.

The former pyknometer values for potassium, rubidium, and cæsium copper sulphates were 2·224, 2·570, and 2·854 respectively. There is every reason for confidence that the new values now given are nearer the truth.

The next table presents the whole of the volume constants of the four copper-containing salts in comparative form. It shows that the molecular volume of the ammonium salt is almost identical with that of the rubidium salt, and in this case very slightly lower. As regards topic axial ratios, the χ and ψ values are slightly lower, and the ω value somewhat higher, than the corresponding values for the rubidium salt.

VOLUME Constants of the Copper Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				$\chi : \psi : \omega$
KCu sulphate . .	438·76	2·233	196·49	6·0709 : 8·1053 : 4·1240
RbCu ,, . .	530·86	2·574	206·24	6·2017 : 8·2800 : 4·1640
NH_4Cu ,, . .	396·92	1·926	206·08	6·1786 : 8·2790 : 4·1942
CsCu ,, . .	624·86	2·858	218·64	6·3332 : 8·5249 : 4·2164

Optics.

Orientation of the Optical Ellipsoid.—The plane of the optic axes is the symmetry plane $b\{010\}$, as usual throughout the series; but the double refraction is by exception of negative sign, the first median line corresponding to the refractive index and axis of indicatrix α, and the second median line to γ. A pair of section-plates ground parallel to the symmetry plane $b\{010\}$ afforded the following extinction angles:—

Inclination of 1st M.L. *from normal to* $c\{001\}$.

Plate 1 . . . 2° 26′ Plate 2 . . . 2° 50′

Mean . . . 2° 38′.

The direction is (by exception in the series) in front of the normal, away from the axis c. MURMANN and ROTTER observed the same fact and found the angle from the normal 2° 33′.

As the axial angle $ac = 73° 51'$, this direction, which is that of the first and not the second median line (the double refraction being negative), is 18° 47′ from (in front of) the vertical axis c, and the other extinction in the symmetry plane is 2° 38′ from (below) the axis a. The two mutually perpendicular extinction directions in the symmetry plane are thus not both in the obtuse angle of the morphological axes ac (as is the case in other groups than the copper group). The positions of the four optical ellipsoids of the copper group of salts are given in the next table, and expressed in fig. 10.

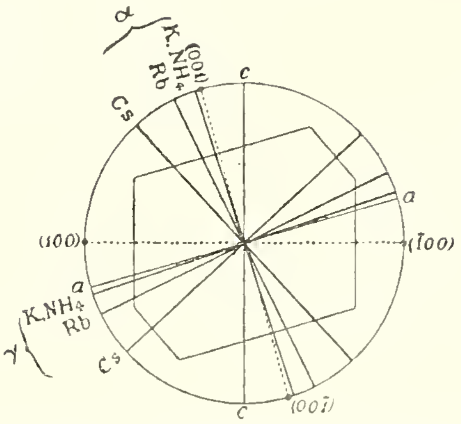

Fig. 10.

Inclinations of α-Extinctions of the Copper Salt in front of Axis c.

(1M.L. *in* Am *salt and* 2M.L. *in other three salts*).

AmCu sulphate	18° 47′	RbCu sulphate	26° 28′
KCu ,,	18° 33′	CsCu ,,	42° 57′.

In this case of the copper group the ellipsoid of the ammonium salt is almost identically situated with the potassium salt, whereas in other groups it has not been inclined so much as the potassium salt from the vertical position. The whole of the positions of the ellipsoid (as indicated by its α-axis) for the four copper salts are considerably further forward than in the other groups.

Refractive Indices.—The next table gives the results of the refractive index determinations, carried out with six excellent 60°-prisms, each ground so as to afford two indices directly.

Refractive Indices of Ammonium Copper Sulphate.

Light.	α.	β.	γ.
Li	1·4878	1·4972	1·5020
C	1·4883	1·4977	1·5025
Na	1·4910	1·5007	1·5054
Tl	1·4938	1·5035	1·5083
Cd	1·4954	1·5052	1·5099
F	1·4971	1·5067	1·5116
G	1·5024	1·5121	1·5171

Mean of α, β, and γ for Na light = 1·4990.

α = Vibration direction parallel to first median line, 18° 47′ in front of axis c.
β = ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, second median line.

Murmann and Rotter obtained indirectly values for the β index varying from 1·494 for red light to 1·502 for blue light.

General Formula for β (corrected to a vacuum):—

$$\beta = 1{\cdot}4809 + \frac{904\,205}{\lambda^2} - \frac{7\,045\,250\,000\,000}{\lambda^4} + \dots$$

The α indices are also reproduced by the formula if the constant 1·4809 is diminished by 0·0096, and the γ indices if it is increased by 0·0048.

Observations at 70° indicated that for 55° rise of temperature the refractive indices are diminished by about 0·0027 for γ, but only by 0·0005 for α, and by an intermediate amount for β, the β index approaching nearer to the midway position between the α and γ indices.

The refractive indices of the four salts containing copper are compared in the next table.

Comparison of the Refractive Indices.

Index.	Light.	KCu sulphate.	RbCu sulphate.	NH_4Cu sulphate.	CsCu sulphate.
α	Li	1·4807	1·4858	1·4878	1·5017
	C	1·4811	1·4862	1·4883	1·5021
	Na	1·4836	1·4886	1·4910	1·5048
	Tl	1·4861	1·4912	1·4938	1·5074
	F	1·4893	1·4943	1·4971	1·5108
	G	1·4944	1·4991	1·5024	1·5159
β	Li	1·4834	1·4878	1·4972	1·5032
	C	1·4838	1·4882	1·4977	1·5036
	Na	1·4864	1·4906	1·5007	1·5061
	Tl	1·4889	1·4933	1·5035	1·5089
	F	1·4922	1·4966	1·5067	1·5123
	G	1·4975	1·5013	1·5121	1·5174
γ	Li	1·4990	1·5007	1·5020	1·5122
	C	1·4994	1·5011	1·5025	1·5126
	Na	1·5020	1·5036	1·5054	1·5153
	Tl	1·5047	1·5064	1·5083	1·5180
	F	1·5081	1·5098	1·5116	1·5216
	G	1·5134	1·5148	1·5171	1·5266
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4907	1·4943	1·4990	1·5087
Double refraction, $Na_{\gamma-\alpha}$		0·0184	0·0150	0·0144	0·0105

It will be clear from this table that the refractive indices of ammonium copper sulphate are slightly higher than those of rubidium copper sulphate; the mean refractive index at the foot of the table shows this well. The double refraction is also only slightly different from (beyond) that of the rubidium salt, being slightly less, this property being a diminishing one while refractive index is an increasing property as the alkali-metal series is ascended.

Axial Ratios of the Optical Ellipsoid.—The calculated values of these ratios, both for the ammonium salt now described and for the analogous salts of the alkali metals previously studied, are collated comparatively in the next table.

AXIAL Ratios of the Optical Indicatrix.

	$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KCu sulphate . . .	0·9981 : 1 : 1·0105	0·9981 : 1 : 1·0105
RbCu ,, . . .	0·9987 : 1 : 1·0087	1·0015 : 1·0028 : 1·0116
NH_4Cu ,, . . .	0·9936 : 1 : 1·0031	1·0031 : 1·0096 : 1·0128
CsCu ,, . . .	0·9991 : 1 : 1·0061	1·0124 : 1·0132 : 1·0194

AXIAL Ratios of the Optical Velocity Ellipsoid.

	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$
KCu sulphate . . .	1·0019 : 1 : 0·9896	1·0019 : 1 : 0·9896
RbCu ,, . . .	1·0013 : 1 : 0·9914	0·9985 : 0·9972 : 0·9886
NH_4Cu ,, . . .	1·0065 : 1 : 0·9969	0·9969 : 0·9905 : 0·9874
CsCu ,, . . .	1·0009 : 1 : 0·9939	0·9878 : 0·9869 : 0·9809

Here again, as regards the absolute dimensions of the optical ellipsoid along its three axial directions, as indicated by the right-hand series of ratios, the ammonium salt stands just beyond the rubidium salt. In the left-hand series, in which the β axis of each salt is the reference dimension for that salt, the copper group shows its individuality in the fact that the ratios for the ammonium salt are the lowest or highest, instead of, as in the other groups, being intermediate between the values for the rubidium and cæsium salts.

Molecular Optical Constants.—These are set forth in the next three tables, for all four salts, the new values now given for the densities having been employed in recalculating the values for the three salts containing the alkali metals.

The specific refraction and dispersion of the ammonium salt stand out prominently higher than those of the three alkali-metal salts. The molecular dispersion for the ammonium salt is not, in this group by exception, the highest, but stands below, yet nearest to, that for the cæsium salt.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.						Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmCu . . .	0·1497	0·1521	0·1534	0·1533	0·1558	0·1571	0·0036	0·0037	0·0037
KCu	0·1275	0·1281	0·1316	0·1305	0·1312	0·1347	0·0030	0·0031	0·0031
RbCu . . .	0·1116	0·1120	0·1145	0·1141	0·1145	0·1171	0·0025	0·0025	0·0026
CsCu . . .	0·1033	0·1035	0·1051	0·1057	0·1059	0·1075	0·0024	0·0024	0·0024

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2}\cdot\frac{M}{d}=\mathfrak{m}$.						Molecular dispersion, $\mathfrak{m}_G-\mathfrak{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KCu sulphate	55·93	56·20	57·73	57·24	57·55	59·09	1·31	1·35	1·36
RbCu ,,	59·23	59·44	60·77	60·57	60·79	62·17	1·34	1·35	1·40
AmCu ,,	59·41	60·38	60·87	60·86	61·85	62·35	1·45	1·47	1·48
CsCu ,,	64·53	64·70	65·67	66·02	66·19	67·18	1·49	1·49	1·51

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KCu sulphate	94·53	95·06	98·13	95·91
RbCu ,, ...	100·27	100·69	103·35	101·44
AmCu ,, ...	100·63	102·57	103·56	102·25
CsCu ,, ...	109·78	110·11	112·07	110·65

As regards the important property of molecular refraction the copper group shows the same relation as the other groups, namely, that the values for the ammonium salt are slightly higher than those for the rubidium salt, as is well expressed in the last column of the third table by the mean molecular refraction.

Optic Axial Angle.—Three pairs of section plates, parallel to the first and second median lines, afforded the following results :—

APPARENT Optic Axial Angle in Air, 2E, of AmCu Sulphate.

Light.	Plate 1.	Plate 2.	Plate 3.	Mean 2E.
	° ′	° ′	° ′	° ′
Li	116 41	115 45	116 20	116 15
C	116 20	115 27	116 0	115 56
Na	115 18	113 43	114 46	114 36
Tl	114 19	112 50	113 40	113 36
Cd	113 32	112 0	113 9	112 54
F	113 12	111 30	112 45	112 29

A determination with Plate 3 at temperatures up to 65° indicated that 2E increases rapidly on rise of temperature, a fact which accords with the alteration of the refractive indices by rise of temperature.

For Na light the angle at the ordinary temperature, 15°, was 114° 46′, at 40° it had increased to 131° 15′, at 45° to 136°, at 50° to 138°, at 55° to 143°, and at 65° to 158° 20′. The angle thus increases by 44° for 50° rise of temperature.

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	61 56	1*a*	96 31	69 11	69 1
	2	61 25	2*a*	96 30	68 47	
	3	61 45	3*a*	96 25	69 5	
C	1	61 52	1*a*	96 30	69 8	68 57
	2	61 23	2*a*	96 30	68 46	
	3	61 35	3*a*	96 25	68 57	
Na	1	61 3	1*a*	96 26	68 32	68 31
	2	60 50	2*a*	96 30	68 20	
	3	60 50	3*a*	96 25	68 22	
Tl	1	60 4	1*a*	96 21	67 46	67 40
	2	59 58	2*a*	96 30	67 38	
	3	59 52	3*a*	96 25	67 35	
Cd	1	59 42	1*a*	96 18	67 30	67 16
	2	59 18	2*a*	96 30	67 6	
	3	59 24	3*a*	96 25	67 13	
F	1	59 18	1*a*	96 14	67 12	66 55
	2	58 45	2*a*	96 30	66 39	
	3	59 0	3*a*	96 25	66 53	

Section 1*a* showed clear although minute dispersion, but Sections 2*a* and 3*a* showed no trace of dispersion, the brushes in white light being sharply black without trace of coloured borders.

MURMANN and ROTTER found by indirect observation 121° 39′ for 2E, and 71° 21′ for $2V_a$.

Dispersion of the Median Lines.—The inclined dispersion is very minute. Measurements in toluene indicated that the first median line lies nearer to the axis *c* for red Li light by 7′ (mean of 4′, 10′, and 6′) than for greenish-blue F light.

In the next table the optic axial angles of the four copper salts are compared. The ammonium salt is seen to display an essential difference from the alkali-metal salts as regards optic axial angle.

Optic Axial Angles $2V_a$ of the Copper Group.

	AmCu sulphate.	KCu sulphate.	RbCu sulphate.	CsCu sulphate.
	° ′	° ′	° ′	° ′
Li	69 1	46 1	44 26	43 6
C	68 57	46 6	44 29	43 9
Na	68 31	46 32	44 42	43 24
Tl	67 40	47 0	44 57	43 40
F	66 55	47 33	45 15	44 3

Ammonium Cadmium Sulphate, $(NH_4)_2Cd(SO_4)_2 . 6H_2O$.

This salt is not included in the investigations of Murmann and Rotter, but a few measurements of the crystals are given by Rammelsberg,* and these values are appended in the last column of the table of angles given on next page. All the forms given in the list of "forms observed" below were also observed by Rammelsberg.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Ratios of Axes.—

$a : b : c = 0·7364 : 1 : 0·4931$. Values of Rammelsberg, 0·7431 : 1 : 0·4945.

Axial Angle.—$\beta = 106° 41'$. Value of Rammelsberg, 107° 23′.

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $p'''\{130\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o\{111\}$, $o'\{\bar{1}11\}$.

Habit.—Prismatic parallel to the axis c, sometimes fairly long as in fig. 11, but more frequently short and almost tabular parallel to $c\{001\}$ as in fig. 12.

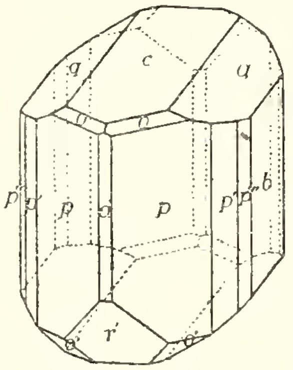

Fig. 11.

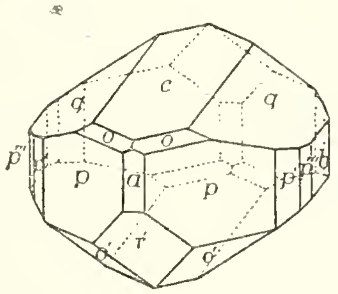

Fig. 12.

The crystals of this salt are exceptionally rich in faces, practically all the ten crystals measured exhibiting all the forms enumerated in the above list. They are less transparent than those of the other salts, being a translucent white. For this reason their optical investigation has presented considerable difficulty, and for the purpose of

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* 'Handb. der Krystall.-phys. Chemie,' Leipzig, 1881, 1, 460.

INTERFACIAL Angles of Ammonium Cadmium Sulphate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of RAMMELSBERG.
$ac = (100):(001)$	16	73° 5′– 73° 28′	73° 16′	73° 19′	3′	72° 37′
$as = (100):(101)$	—	—	—	45 5	—	—
$sc = (101):(001)$	—	—	—	28 14	—	—
$cr' = (001):(\bar{2}01)$	18	64 8– 64 29	64 22	64 18	4	64 50
$cs' = (001):(\bar{1}01)$	—	—	—	38 23	—	—
$s'r' = (\bar{1}01):(\bar{2}01)$	—	—	—	25 55	—	—
$r'a = (\bar{2}01):(\bar{1}00)$	15	42 11– 42 25	42 19	42 23	4	—
$ap = (100):(110)$	21	35 3– 35 24	35 13	35 14	1	—
$pp' = (110):(120)$	21	19 10– 19 37	19 24	19 28	4	19 28
$p'b = (120):(010)$	21	35 9– 35 34	35 23	35 18	5	—
$p'p''' = (120):(130)$	13	9 52– 10 17	10 5	10 2	3	—
$pp''' = (110):(130)$	16	29 16– 29 46	29 29	29 30	1	29 30
$p'''b = (130):(010)$	18	25 7– 25 27	25 17	25 16	1	—
$pb = (110):(010)$	26	54 36– 54 57	54 46	*	—	—
$pp = (110):(1\bar{1}0)$	17	70 18– 70 37	70 26	70 28	2	70 36
$cq = (001):(011)$	32	25 4– 25 26	25 17	25 17	0	25 11
$qb = (011):(010)$	31	64 32– 64 54	64 43	*	—	—
$ao = (100):(111)$	14	48 1– 48 25	48 10	48 12	2	—
$oq = (111):(011)$	19	26 33– 27 1	26 47	26 45	2	—
$aq = (100):(011)$	23	74 36– 75 11	74 55	74 57	2	74 45
$qo' = (011):(\bar{1}11)$	24	34 36– 34 57	34 47	34 43	4	34 35
$o'a = (\bar{1}11):(\bar{1}00)$	21	70 0– 70 28	70 16	70 20	4	—
$co = (001):(111)$	27	33 25– 33 56	33 42	33 43	1	33 30
$op = (111):(110)$	25	42 30– 42 58	42 44	42 43	1	—
$cp = (001):(110)$	35	76 18– 76 43	76 26	*	—	—
$po' = (110):(11\bar{1})$	32	58 40– 59 5	58 53	59 0	7	59 39
$o'c = (11\bar{1}):(00\bar{1})$	33	44 25– 44 57	44 41	44 34	7	44 42
$bn = (010):(121)$	—	—	—	55 4	—	—
$no = (121):(111)$	—	—	—	15 41	—	—
$bo = (010):(111)$	19	70 31– 70 55	70 46	70 45	1	—
$os = (111):(101)$	—	—	—	19 15	—	—
$oo = (111):(1\bar{1}1)$	8	38 14– 38 38	38 28	38 30	2	—
$bo' = (010):(\bar{1}11)$	29	65 11– 65 30	65 24	65 23	1	—
$o's' = (\bar{1}11):(\bar{1}01)$	—	—	—	24 37	—	—
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$	13	49 0– 49 20	49 12	49 14	2	—
$sq = (101):(011)$	—	—	—	37 11	—	—
$qp = (011):(\bar{1}10)$	28	87 54– 88 8	88 2	88 2	0	—
$ps = (\bar{1}10):(\bar{1}0\bar{1})$	—	—	—	54 47	—	—
$pq = (\bar{1}10):(0\bar{1}\bar{1})$	26	91 50– 92 7	91 58	91 58	0	—
$s'q = (\bar{1}01):(011)$	—	—	—	44 52	—	—
$qn = (011):(121)$	—	—	—	26 9	—	—
$np = (121):(110)$	—	—	—	36 34	—	—
$qp = (011):(110)$	31	62 31– 62 59	62 42	62 43	1	—
$ps' = (110):(10\bar{1})$	—	—	—	72 25	—	—
$pq = (110):(0\bar{1}\bar{1})$	30	117 4–117 30	117 17	117 17	0	—
$r'o' = (\bar{2}01):(\bar{1}11)$	30	34 45– 35 24	35 6	35 9	3	—
$o'p = (\bar{1}11):(110)$	28	91 52– 92 17	92 3	91 58	5	—
$pr' = (110):(20\bar{1})$	30	52 37– 52 58	52 49	52 53	4	—
Total number of measurements . .	790					

density determinations the crystals have had to be freshly prepared and used very soon after removal from the mother liquor. Their goniometrical measurement, however, has offered no difficulty.

The relative development of the faces is frequently so different from the main types illustrated in figs. 11 and 12, that it is not always easy to recognise the various faces immediately. The ten small crystals measured were selected from the two best crops of a very large number prepared. They afforded very satisfactory goniometrical results (see accompanying table of angles) in all cases but those involving the faces of $o'\{\bar{1}11\}$ in the zone $[cpo']$; for when this zone was adjusted these faces invariably showed multiple images of the signal, due to more or less striation, so that the mean measured values of the angles po' and $o'c$ differed rather more than usual from the calculated values.

The rarer forms common to this monoclinic series of double salts are exceptionally well developed on the crystals of cadmium ammonium sulphate; for instance, the faces of $a\,\{100\}$, $o\,\{111\}$, $p'\{120\}$, and $p'''\{130\}$ have been frequently observed quite large. Moreover, single faces of the commoner forms $b\,\{010\}$ and $r'\{\bar{2}01\}$ are occasionally found phenomenally developed; thus several crystals were found roughly hemispherical, the large flat base being a particularly large and perfectly plane b-face, while others were found with a similarly predominatingly developed r'-face.

The morphological constants of the three cadmium-containing salts are compared in the next two tables. As already explained, potassium cadmium sulphate with $6H_2O$ has so far resisted all attempts at preparation. The first table shows that the axial ratios of the ammonium cadmium salt are very close to those of the rubidium cadmium salt. The axial angle β of the ammonium salt is not far removed from that of the cæsium salt, but is not so close as in all the other groups investigated. The morphological angles of the ammonium salt are shown in the second table to be related to those of the rubidium and cæsium salts in a very similar manner to what has been shown to occur in the other groups, for which it has been possible to effect a complete comparison and to determine the differences in angle of all three salts from the potassium salt. They indicate conclusively that the ammonium salt belongs to the same isomorphous series as the rubidium and cæsium salts containing cadmium.

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Rubidium cadmium sulphate .	105° 53′	0·7346 : 1 : 0·4931
Ammonium ,, ,, .	106° 41′	0·7364 : 1 : 0·4931
Cæsium ,, ,, .	107° 11′	0·7259 : 1 : 0·4906

Comparison of the Interfacial Angles.

Angle.	RbCd sulphate.	CsCd sulphate.	AmCd sulphate.
	° ′	° ′	° ′
$ac = (100) : (001)$	74 7	72 49	73 19
$as = (100) : (101)$	45 29	44 31	45 5
$sc = (101) : (001)$	28 38	28 18	28 14
$cr' = (001) : (\bar{2}01)$	63 56	65 5	64 18
$cs' = (001) : (\bar{1}01)$	38 22	38 54	38 23
$s'r' = (\bar{1}01) : (\bar{2}01)$	25 34	26 11	25 55
$r'a = (\bar{2}01) : (\bar{1}00)$	41 57	42 6	42 23
$ap = (100) : (110)$	35 14	34 44	35 14
$pp' = (110) : (120)$	19 28	19 28	19 28
$p'b = (120) : (010)$	35 18	35 48	35 18
$pb = (110) : (010)$	54 46	55 16	54 46
$cq = (001) : (011)$	25 24	25 8	25 17
$qb = (011) : (010)$	64 36	64 52	64 43
$ao = (100) : (111)$	48 35	47 37	48 12
$oq = (111) : (011)$	27 6	26 52	26 45
$aq = (100) : (011)$	75 41	74 29	74 57
$qo' = (011) : (\bar{1}11)$	34 41	35 11	34 43
$o'a = (\bar{1}11) : (\bar{1}00)$	69 38	70 20	70 20
$co = (001) : (111)$	34 6	33 38	33 43
$op = (111) : (110)$	42 59	42 19	42 43
$cp = (001) : (110)$	77 5	75 57	76 26
$po' = (110) : (11\bar{1})$	58 26	59 8	59 0
$o'c = (11\bar{1}) : (00\bar{1})$	44 29	44 55	44 34
$bo = (010) : (111)$	70 38	71 1	70 45
$os = (111) : (101)$	19 22	18 59	19 15
$bo' = (010) : (\bar{1}11)$	65 30	65 30	65 23
$o's' = (\bar{1}11) : (\bar{1}01)$	24 30	24 30	24 37
$sq = (101) : (011)$	37 33	37 9	37 11
$qp = (011) : (\bar{1}10)$	87 23	88 43	88 2
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	55 4	54 8	54 47
$s'q = (\bar{1}01) : (011)$	44 54	45 12	44 52
$qp = (011) : (110)$	63 18	62 30	62 43
$ps' = (110) : (10\bar{1})$	71 48	72 18	72 25
$r'o' = (\bar{2}01) : (\bar{1}11)$	34 50	35 15	35 9
$o'p = (\bar{1}11) : (110)$	92 35	92 19	91 58
$pr' = (110) : (20\bar{1})$	52 35	52 26	52 53

Cleavage.—A fairly good cleavage parallel to *r′* $\{\bar{2}01\}$ is developed in the crystals of ammonium cadmium sulphate. No trace of cleavage parallel to *b* $\{010\}$ was discovered.

Volume.

Relative Density.—Four determinations by the immersion method gave the following results :—

I.	Density for	13°·6/4°	2·0613	For	20°/4°	2·0600
II.	,,	14°·2/4°	2·0620	,,	20°/4°	2·0608
III.	,,	13°·9/4°	2·0623	,,	20°/4°	2·0610
IV.	,,	13°·5/4°	2·0631	,,	20°/4°	2·0618
				Mean		2·0609

Accepted value for 20°/4°, **2·061**.

Molecular Volume.—$\frac{M}{d} = \frac{445·42}{2·061} = 216·12$.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6·2838 : 8·5332 : 4·2078.$$

Redeterminations of Densities of Rubidium and Cæsium Cadmium Sulphates.

Rubidium Cadmium Sulphate, $Rb_2 Cd (SO_4)_2 . 6H_2O$.

I.	Density for	15°·6/4°	2·6963	For	20°/4°	2·6951
II.	,,	15°·8/4°	2·6976	,,	20°/4°	2·6965
III.	,,	15°·3/4°	2·6984	,,	20°/4°	2·6972
IV.	,,	15°·0/4°	2·6942	,,	20°/4°	2·6928
V.	,,	16°·0/4°	2·6946	,,	20°/4°	2·6935
				Mean		2·6950

Accepted value for 20°/4°, **2·695**.

Cæsium Cadmium Sulphate, $Cs_2 Cd (SO_4)_2 . 6H_2O$.

I.	Density for	14°·8/4°	2·9582	For	20°/4°	2·9568
II.	,,	15°·6/4°	2·9572	,,	20°/4°	2·9560
III.	,,	14°·8/4°	2·9567	,,	20°/4°	2·9553
IV.	,,	14°·7/4°	2·9593	,,	20°/4°	2·9578
				Mean		2·9565

Accepted value for 20°/4°, **2·957**.

The former values for the pyknometer method were 2·672 for the rubidium salt, and 2·955 for the cæsium salt.

As was fully described in the communication describing the work on rubidium cadmium sulphate,[*] special difficulties were found in carrying out density determina-

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[*] 'Journ. Chem. Soc., Trans.,' 1896, 69, 445.

tions of this salt by the pyknometer method, owing to rapid efflorescence, which was greatly accelerated by powdering and necessitated rapid working and weighing while covered with carbon tetrachloride, the pyknometer liquid. The immersion method is free from the powdering difficulty, and it is only necessary to use freshly grown crystals, and to preserve them under benzene until the moment of dropping them into the immersion liquid mixture of methylene iodide and benzene. This was done in the cases of the five determinations now recorded, and the result, 2·695, is much higher than the former pyknometer one, and can be accepted with confidence.

VOLUME Constants of the Cadmium Group.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				$\chi : \psi : \omega$
RbCd sulphate . .	579·36	2·695	214·98	6·2539 : 8·5133 : 4·1980
NH_4Cd ,, . .	445·42	2·061	216·12	6·2838 : 8·5332 : 4·2078
CsCd ,, . .	673·36	2·957	227·72	6·3497 : 8·7472 : 4·2914

The comparative table of the volume constants shows that the ammonium cadmium salt occupies a position just beyond that of the rubidium cadmium salt, the molecular volume and all three topic axial ratios being slightly higher.

Optics.

No optical investigation of this salt appears to have been hitherto undertaken. It is a matter of some difficulty, as ground surfaces of the crystals effloresce with great rapidity; also the use of warm wax on the crystal holder for cementing purposes is precluded, as rise of temperature provokes instant opacity from loss of water of crystallisation. By careful rapid work, however, the use of a special wax, and immediately covering ground surfaces with very thin truly plane glass plates cemented by hard balsam in benzene, all these difficulties were eventually overcome.

Orientation of Optical Ellipsoid.—The optic axes lie in the symmetry plane b {010} and the sign of the double refraction is positive. The first median line corresponds to the axis γ of the optical indicatrix and the second median line to α.

A pair of section-plates parallel to the symmetry plane afforded the extinction angles:—

Inclination of 2M.L. *from normal to* c {001}.

Plate 1 . . . 5° 8′ Plate 2 . . . 5° 20′

Mean . . . 5° 14′.

The direction is behind the normal. As the axial angle $ac = 73° \ 19'$ this extinction direction, the second median line, is 11° 27′ from and in front of the vertical axis c; and the other extinction in the symmetry plane, the first median line, is 5° 14′ from and above the axis a, both median lines thus lying in the obtuse angle of the morphological axes ac.

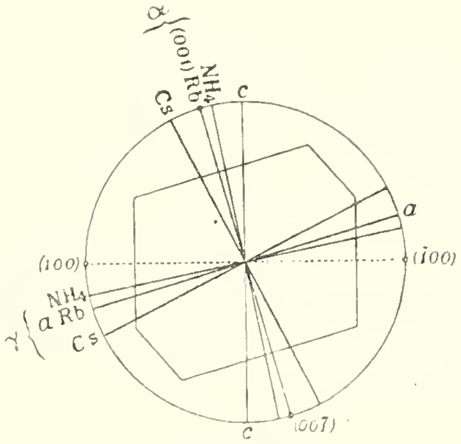

Fig. 13.

The positions of the optical indicatrix for the three cadmium salts are compared in the next table, and illustrated in fig. 13.

Inclinations of α-Axis of the Indicatrix (2M.L.) *of the Cadmium Salts in front of Axis c.*

AmCd sulphate		11° 27′
RbCd	,,	15° 53′
CsCd	,,	26° 56′

The order of these positions of the indicatrix for the three salts is similar to what has been observed in the other groups, in which the potassium salt also has been able to be compared.

Refractive Indices.—Determinations with six prisms, each ground to yield two indices directly, gave the results summarised in the accompanying table.

Refractive Indices of Ammonium Cadmium Sulphate.

Light.	α.	β.	γ.
Li	1·4816	1·4855	1·4927
C	1·4821	1·4860	1·4932
Na	1·4847	1·4887	1·4959
Tl	1·4875	1·4915	1·4987
Cd	1 4891	1·4931	1·5003
F	1·4907	1·4947	1·5019
G	1·4961	1·5001	1·5073

Mean of α, β, and γ for Na light = 1·4898.

α = Vibration-direction parallel to second median line, 11° 27′ in front of axis c.
β = ,, ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, ,, first median line.

General formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}4736 + \frac{605\,763}{\lambda^2} - \frac{2\,351\,170\,000\,000}{\lambda^4} + \ldots .$$

The α indices are equally well reproduced by the formula if the constant 1·4736 is diminished by 0·0040, and the γ indices if it is increased by 0·0072.

Observations at higher temperatures were precluded on account of decomposition and opacity due to loss of water of crystallisation.

In the next table the refractive indices of the three cadmium-containing salts are compared.

COMPARISON of the Refractive Indices.

Index.	Light.	RbCd sulphate.	NH_4Cd sulphate.	CsCd sulphate.
α	Li	1·4773	1·4816	1·4947
	C	1·4777	1·4821	1·4951
	Na	1·4798	1·4847	1·4975
	Tl	1·4823	1·4875	1·5000
	F	1·4856	1·4907	1·5033
	G	1·4906	1·4961	1·5081
β	Li	1·4820	1·4855	1·4972
	C	1·4824	1·4860	1·4976
	Na	1·4848	1·4887	1·5000
	Tl	1·4872	1·4915	1·5026
	F	1·4905	1·4947	1·5058
	G	1·4955	1·5001	1·5106
γ	Li	1·4919	1·4927	1·5034
	C	1·4923	1·4932	1·5038
	Na	1·4948	1·4959	1·5062
	Tl	1·4972	1·4987	1·5088
	F	1·5097	1·5019	1·5123
	G	1·5061	1·5073	1·5172
Mean refractive index $\frac{1}{3}(\alpha+\beta+\gamma)$ for Na light		1·4865	1·4898	1·5012
Double refraction, $Na_{\gamma-\alpha}$		0·0150	0·0112	0·0087

The refractive indices of the ammonium cadmium salt are just slightly higher than those of the rubidium cadmium salt, the relationship being best expressed by the mean index given at the foot of the table. The double refraction of the ammonium salt is also intermediate between the values for the rubidium and cæsium salts, but in this case nearer to the cæsium salt.

Axial Ratios of the Optical Ellipsoid.—The values of these ratios are compared in the next table. The potassium salt not being available for comparison, only the ratios on the basis of the β value of each salt = 1 are possible.

	AXIAL Ratios of	
	Optical Indicatrix	Optical Velocity Ellipsoid.
	$\alpha : \beta : \gamma$	$\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$
RbCd sulphate . . .	0·9966 : 1 : 1·0067	1·0034 : 1 : 0·9933
NH_4Cd ,, ...	0·9973 : 1 : 1·0048	1·0027 : 1 : 0·9952
CsCd ,, ...	0·9983 : 1 : 1·0041	1·0017 : 1 : 0·9959

The values for the ammonium salt are intermediate between those for the rubidium and cæsium salts.

Molecular Optical Constants.—The next three tables set forth these constants for all three salts of the cadmium group in comparative form. In recalculating the values for the rubidium and cæsium salts the new values for the densities now determined by the immersion method were employed. From the tables it may be deduced that the specific refraction and dispersion of the ammonium salt stand out prominently higher than those of the rubidium and cæsium salts; the molecular dispersion of the ammonium salt also slightly exceeds that of cæsium cadmium sulphate. As regards the most important molecular refraction, all the values for the ammonium salt, including the mean molecular refraction, are just slightly higher than the corresponding values for the rubidium salt. It is immaterial whether the formula of LORENZ or that of GLADSTONE and DALE is employed.

TABLE of Specific Refraction and Dispersion (LORENZ).

Sulphate.	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.						Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmCd . . .	0·1383	0·1393	0·1411	0·1418	0·1427	0·1445	0·0035	0·0034	0·0034
RbCd . . .	0·1050	0·1058	0·1077	0·1074	0·1083	0·1103	0·0024	0·0025	0·0026
CsCd . . .	0·0986	0·0991	0·1001	0·1008	0·1012	0·1023	0·0022	0·0021	0·0022

TABLE of Molecular Refraction and Dispersion (LORENZ).

Salt.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.						Molecular dispersion. $\mathfrak{m}_G - \mathfrak{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
RbCd sulphate	60·82	61·32	62·40	62·22	62·75	63·88	1·40	1·43	1·48
AmCd ,,	61·62	62·05	62·83	63·14	63·57	64·35	1·52	1·52	1·52
CsCd ,,	66·42	66·70	67·41	67·89	68·17	68·92	1·47	1·47	1·51

MOLECULAR Refraction (GLADSTONE and DALE).

Salt.	$\frac{n-1}{d}$ M for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
RbCd sulphate	102·70	103·71	105·83	104·08
AmCd ,, ...	104·19	105·03	106·59	105·27
CsCd ,, ...	112·74	113·31	114·73	113·59

Optic Axial Angle.—Three pairs of section-plates perpendicular to the two median lines were, after much trouble, obtained by grinding, which were adequately transparent to enable a complete series of measurements to be obtained of 2Ha and 2Ho in bromonaphthalene, and the measurement in two cases of 2E for the most brilliant sodium light wave-length. Observations of the dispersion of the median lines between Li and F light were also successfully carried out. The results are shown in the next two tables.

APPARENT Optic Axial Angle in Air, 2E, of AmCd Sulphate for Sodium Light.

Plate 1 . . . 124° 33′ Plate 2 . . . 124° 31′

Mean 2E . . . 124° 32′

DETERMINATION of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	64 29	1*a*	92 48	72 46	72 45
	2	64 27	2*a*	92 57	72 40	
	3	64 32	3*a*	92 44	72 50	
C	1	64 28	1*a*	92 43	72 47	72 46
	2	64 25	2*a*	92 53	72 41	
	3	64 30	3*a*	92 38	72 51	
Na	1	64 16	1*a*	92 18	72 50	72 51
	2	64 11	2*a*	92 20	72 45	
	3	64 16	3*a*	91 58	72 58	
Tl	1	64 0	1*a*	91 43	72 53	72 56
	2	63 57	2*a*	91 46	72 50	
	3	64 2	3*a*	91 22	73 4	
Cd	1	63 48	1*a*	91 22	72 54	72 58
	2	63 50	2*a*	91 23	72 54	
	3	63 54	3*a*	91 4	73 7	
F	1	63 35	1*a*	90 58	72 56	73 1
	2	63 40	2*a*	91 3	72 57	
	3	63 44	3*a*	90 40	73 10	

Dispersion of the Median Lines.—The inclined dispersion is very minute. From observations in toluene with sections 1 and 2 it was ascertained that the first median line lies 8′ nearer to the axis a for Li red light than for greenish-blue F light.

In the next table the optic axial angles of the three cadmium salts are compared.

OPTIC Axial Angles $2V_a$ of the Cadmium Group.

	AmCd sulphate.	RbCd sulphate.	CsCd sulphate.
	° ′	° ′	° ′
Li	72 45	72 20	68 4
C	72 46	72 21	68 2
Na	72 51	72 26	67 53
Tl	72 56	72 31	67 44
F	73 1	72 37	67 28

It will be observed that the optic axial angle of the ammonium cadmium salt is only very slightly larger than that of the rubidium cadmium salt.

Summary of Conclusions.

The results of this investigation of the five remaining ammonium salts of the double sulphate series are perfectly in line with and fully confirm those already derived, in two former communications, from a study of three other ammonium salts of the series. The chief conclusion is that the close similarity of the crystal angles, the axial ratios, the volume constants, and the optical constants of these ammonium salts clearly entitles them to places in the monoclinic isomorphous series $R_2M(SO_4)_2 . 6H_2O$, R being represented by the NH_4 radicle; but that they are not so definitely related, "eutropic" as it has been termed, as are those salts of the series in which R is potassium, rubidium, or cæsium. Now interchange of these R-metals has been shown to exert a comparatively great and dominating effect on the properties of the crystals, progressively with their atomic weights, while change of the M-metal only produces slight change. But this law of progression of the crystallographic properties, both morphological and physical, with the atomic weight of the alkali metal R, which law is the essence of "eutropism," cannot apply as regards ammonium; for we are here dealing with a radicle group of elements, NH_4, and not with three simple interchangeable elements of the same family group of MENDELEEFF'S table, definitely progressive in atomic weight and in all the properties which accompany atomic weight. Yet the group NH_4 possesses the singular power of chemically replacing these alkali metals in their salts, as also does the metal thallium, which is well known to be of a different nature to the three alkali metals potassium, rubidium, and cæsium. It has now been shown that the replacement occurs in these two non-eutropic cases with surprisingly slight alteration of the morphology of the crystals, the change, in fact, being almost *nil* when rubidium is the alkali metal replaced by either ammonium or thallium. While no clear rule like that of eutropic progression can apply as regards ammonium (or thallium), there are still very definite relationships which have been established as the result of the research now completed, which can best be stated separately for the various properties.

Crystal Angles.—The monoclinic axial angle β of the ammonium salt of any group (set of salts containing the same M-metal) is usually very close to that of the cæsium salt of the same group. In six of the eight groups, those in which all four salts (of NH_4, K, Rb, and Cs) are capable of existence, the difference is less than 10′, and in three cases it does not exceed 2′. The change in this important angle when K is replaced by Rb is usually about a degree, and when Cs replaces K about 2 degrees, the latter being almost exactly twice the former, the angular changes corresponding to the two changes in atomic weight, 46 and 93. The maximum changes observed for the two replacements were 1° 12′ and 2° 20′, in the iron group, the NH_4 replacement in this group causing 2° 18′ of change.

In all the six complete groups 32 to 34 out of 36 different interfacial angles compared (all in which the differences are beyond the range of experimental error) show a change of angle on replacing K by NH_4 in the same direction as if Rb or Cs were introduced instead. The average and maximum amounts of the change when NH_4 replaces K are approximately the same as when K is replaced by Cs, and this amount is twice as great as when Rb replaces K; for the average and maximum changes of angles are directly proportional to the change of atomic weight when one alkali metal is substituted for another. (K = 38·85 when H = 1, Rb = 84·9, and Cs = 131·9, and $\frac{38{\cdot}85+131{\cdot}9}{2} = 85{\cdot}4$; also Rb−K = 46, and Cs−Rb = 47.) The maximum change of angle observed for the replacement of K by Cs occurs in the magnesium group, and is 2° 25′; the replacement of K by NH_4 in the same group provokes a change of nearly the same amount, 2° 18′, while the change for the replacement of K by Rb is exactly half the value for the Cs replacement, namely, 1° 12′. This direct proportionality of the average and maximum change of angle to the change in atomic weight of the alkali metal is one of the most striking and important of all the facts brought to light by this prolonged investigation, and is rendered the more important by the large amounts of these changes. It is also interesting to note that the change (strictly proportional to that in atomic weight) in the most important of the angles, the axial angle β, between the primary orthopinakoid $a\ \{100\}$ and basal plane $c\ \{001\}$, is so large as to be nearly equal to the maximum, and in several groups this angle is actually itself the angle of maximum change. These conclusions are, therefore, far away from any possible experimental error, which at the highest estimate could not exceed 5′ and probably does not exceed 3′.

Axial Ratios.—The ratios of the morphological axes of any ammonium salt of the series are very close to those of the alkali-metal salts of the same group, and usually lie within the limits of the latter. They thus afford very strong evidence of the isomorphism of the ammonium salts with the alkali-metal salts of the group and series.

Cleavage.—The crystals of the whole series of salts show cleavage parallel to the orthopinakoid $r'\{\bar{2}01\}$. Four of the ammonium salts, those of the Mg, Ni, Mn, and Cu groups, show in addition a good cleavage parallel to the symmetry plane $b\,\{010\}$, and in ammonium copper sulphate this cleavage is the more perfect of the two. The introduction of the NH_4 radicle in place of an alkali metal thus appears to affect the cleavage. A similar effect was observed in the simple rhombic sulphates of ammonium and the alkali metals; but in this case it took the form of the suppression in ammonium sulphate of one ($b\,\{010\}$, the more perfect cleavage) of the two cleavages (parallel to $b\,\{010\}$ and $c\,\{001\}$) common to the sulphates of K, Rb, and Cs.

Density and Molecular Volume.—The density of the ammonium salt is the lowest in every group. The molecular volume of the ammonium salt, however, is nearly identical with that of the rubidium salt of the same group; on the average it is just slightly higher, the differences varying from 1·6 above to 0·16 below the value for the rubidium salt. The average difference of molecular volume, for the whole of the double sulphate series, between a K and a Rb salt is 9·55 units, between a K and a NH_4 salt 10·41 units, and between a K and a Cs salt 22·23 units. The change of molecular volume with change of the alkali metal thus follows the order of the atomic weights of the alkali metals, and the absolute amounts are a higher function of the atomic weight than direct proportionality. The two following tables will render these facts clear.

RELATIVE Densities Compared.

M metal.	Density of K salt.	Difference between K and Rb salts.	Density of Rb salt.	Difference between K and NH_4 salts.	Density of NH_4 salt.	Difference between Rb and Cs salts.	Density of Cs salt.	Difference between K and Cs salts.
Ni	2·237	0·349	2·586	−0·314	1·923	0·286	2·872	0·635
Co	2·219	0·348	2·567	−0·318	1·901	0·277	2·844	0·625
Mn	—	—	2·461	—	1·831	0·279	2·740	—
Cu	2·233	0·341	2·574	−0·307	1·926	0·284	2·858	0·625
Cd	—	—	2·695	—	2·061	0·262	2·957	—
Mg	2·034	0·352	2·386	−0·311	1·723	0·290	2·676	0·642
Zn	2·246	0·345	2·591	−0·314	1·932	0·284	2·875	0·629
Fe	2·177	0·341	2·518	−0·313	1·864	0·278	2·796	0·619

MOLECULAR Volumes Compared.

M metal.	Molecular volume of K salt.	Difference between K and Rb salts.	Molecular volume of Rb salt.	Difference between K and NH_4 salts.	Molecular volume of NH_4 salt.	Difference between Rb and Cs salts.	Molecular volume of Cs salt.	Difference between K and Cs salts.
Ni	193·99	9·44	203·43	9·92	203·91	12·47	215·90	21·91
Co	195·68	9·35	205·03	10·72	206·40	13·08	218·11	22·43
Mn	—	—	212·26	—	212·13	12·69	224·95	—
Cu	196·49	9·75	206·24	9·59	206·08	12·40	218·64	22·15
Cd	—	—	214·98	—	216·12	12·74	227·72	—
Mg	196·58	9·60	206·18	11·20	207·78	12·78	218·96	22·38
Zn	196·16	9·42	205·58	10·22	206·38	12·39	217·97	21·81
Fe	198·05	9·76	207·81	10·81	208·86	12·96	220·77	22·72
	Mean . . .	9·55	Mean . . .	10·41	Mean . . .	12·69	Mean . . .	22·23

Molecular Distance Ratios (*topic axial ratios*).—When considered comparatively for the different salts these represent directionally in the crystal the same changes as are represented in total alteration of volume by the comparison of the molecular volumes. The ratios may be regarded as expressing the relative dimensions in space of the unit cells of the space-lattice of the crystal structure, the volume of the cell being expressed by the molecular volume. In the zinc and cadmium groups all three ratios of the ammonium salt are slightly greater than those of the rubidium salt ; in the magnesium, iron, manganese, nickel and cobalt groups χ and ψ are slightly greater and ω slightly less, and in the copper group χ and ψ are slightly less and ω slightly greater. Thus, on the average, just as for the molecular volume, the spatial axial ratios of the ammonium salt are slightly greater than for the intermediate rubidium salt. It will be observed that these results include, and are in agreement with, those previously published for the magnesium, zinc, and iron groups.

It may now, therefore, be stated definitely for the whole series of double sulphates, without exception, that the replacement of potassium by ammonium (K_2 by $2NH_4$) is accompanied by scarcely more change of volume, or change in the directional dimensions of the unit cell of the space-lattice, than when potassium is replaced by rubidium (K_2 by Rb_2), and by only half the change of volume which ensues on the replacement of potassium by cæsium (K_2 by Cs_2). Regarded in another light, the replacement of the two atoms of rubidium by the ten atoms of the two ammonium NH_4 radicle-groups is accompanied by scarcely any appreciable change in the structural dimensions, either molecular volume or topic axial ratios (volume or directional extension).

Orientation of the Optical Ellipsoid.—Throughout the series the optical ellipsoid rotates about the symmetry axis *b*, which is in all cases the intermediate β axis of the ellipsoid, on replacing potassium successively by rubidium and cæsium, the positions following the order of the atomic weights of the alkali metals. The α axis of the ellipsoid is nearest to the vertical axis c of the crystal, and the approximation is closest, among the alkali-metal salts, for the potassium salt. It is even closer, except in the copper group, for the ammonium salt, the potassium salt coming next, then the rubidium salt and the cæsium salt at such angles as accord with the order of the atomic weights, but with a higher function than mere direct proportion to atomic weight. In the copper group the ammonium and potassium salts exhibit optical ellipsoids almost identically situated, with the α axis inclined $18\frac{3}{4}°$ from the vertical axis c, the positions of the ellipsoids of the rubidium and cæsium salts still following the rule of progression.

Refractive Indices.—In all the eight groups the refractive indices, including the mean index, of the ammonium salt are very close to those of the rubidium salt (which are always intermediate between those for the K and Cs salts), and usually very slightly higher. The double refraction of the ammonium salt also lies intermediate between the values for the corresponding rubidium and cæsium salts, the situation varying in the different groups on either side of the half-way position ; on the average it lies nearer to the value for the rubidium salt. As regards the axial ratios (the directional dimensions) of the optical ellipsoid, the values for the ammonium salt of any group are intermediate between the values for the rubidium and cæsium salts of the same group, and much nearer to the rubidium salt values.

Molecular Optical Constants.—In specific refraction and dispersion the ammonium salt of every group is distinguished by values much higher than those for the alkali-metal salts of the same group. As regards the important property of molecular refraction, in every group of the series the value for the ammonium salt, whether calculated by the LORENZ or the GLADSTONE and DALE formula, is very close to and just slightly higher than the value for the rubidium salt, which itself is intermediate between the values for the potassium and cæsium salts, in accordance with the law of progression with the atomic weight of the alkali metal. The molecular dispersion of the ammonium salt is nearest to the value for the corresponding cæsium salt, in four groups being just lower than the latter, and in the other four groups just higher ; for high dispersion is a characteristic property in which the ammonium salts exhibit the constitutional difference of the NH_4 radicle from the alkali metals which form the other R-bases in the isomorphous salts of the series.

Optic Axial Angle.—No definite rule can be traced from a comparison of the optic axial angles of the ammonium salts with those of the salts containing the alkali metals ; these latter salts show a progressive change in optic axial angle with change of atomic weight of the alkali metal.

Final Conclusion.—The work now described on the remaining five double sulphates containing ammonium confirms and emphasises the two main conclusions derived from the study of the three ammonium salts already described, which may be stated as follows:—(1) These ammonium salts are truly isomorphous with the similarly constituted potassium, rubidium, and cæsium salts of the generic formula $R_2M(SO_4)_2 . 6H_2O$, but are not eutropic with them; the potassium, rubidium, and cæsium salts alone form the exclusive eutropic series, in which the crystallographic (morphological and physical) properties obey the law of progression with the atomic weight of the alkali metal, which has been established in the previous communications concerning those salts. This law is particularly well illustrated by the fact, to which no exceptions have been observed, that the average change of angle between the crystal faces, and also the maximum change of interfacial angle (which usually occurs for the all-important monoclinic axial angle between the primary faces, and exceeds between a K and a Cs salt two whole degrees), are directly proportional to the change in atomic weight, when any one alkali metal is replaced by another.

(2) The dimensions of the space-lattice of any ammonium salt of the series are nearly identical with those of the intermediate alkali metal salt, that containing rubidium as the R-metal; so that the two atoms of rubidium are replaced by the ten atoms of the two NH_4 radicle-groups without appreciably altering the crystallographic structural dimensions.

To these may be added the following third general conclusion, which has been substantiated as regards thallium in a former communication*:— (3) The salts of this series in which R is thallium resemble the ammonium salts closely, in truly belonging to the isomorphous series, but not to the more exclusive eutropic series formed by the salts of potassium, rubidium, and cæsium. Like the ammonium salts, the thallium salts also closely resemble the rubidium salts, but the thallium salts are distinguished optically, by their transcendent refractive power, both their refractive indices and their molecular refraction being far higher than for any other salts of the whole isomorphous series.

An interesting memoir has recently appeared by F. M. JAEGER† on the crystallised ethylsulphates of the rare earths, $R_2'''(SO_4 . C_2H_5)_6 + 18H_2O$ in which R is Yt, Ce, La, Nd, Pr, Sm, Eu, Dys, Gd, Er, Thu, and NYb. JAEGER finds that the crystalline forms of these salts are so extremely close to each other that the differences fall within the limits of experimental error. He concludes, therefore, that they are rigorously identical, oscillating about a mean form in a manner entirely accidental. The rare earths, forming a group to themselves, and differing so little (especially in their sub-groups) in the values of their atomic weights, present an altogether different order of problem to the comparison of K, Rb, and Cs compounds. The series of rare earths belong to the central groups of the periodic system, in which the electro-positive property is at its minimum, and the chemical characters are so remarkably alike that extraordinary processes and refinement of method

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* 'Roy. Soc. Proc.' A, 1909, 83, 211.

† 'Recueil des Trav. Chim. des Pays-Bas,' 1914, 33, 343.

are necessary in order to separate their compounds from each other. Extreme closeness of the crystallographic characters of their crystallised salts is, therefore, precisely what one would expect to find. The very opposite is the case for the alkali metals, which latter were chosen expressly by the author (Tutton) as belonging to the first group of the periodic system, exhibiting the electro-positive property at its maximum, while at the same time showing large differences (46 between K and Rb and 47 between Rb and Cs) in atomic weight. Moreover, the crystal system of the ethylsulphates of the rare earths is the hexagonal, and a comprehensive comparison of the author's results on the rhombic (simple sulphates and selenates) and monoclinic (double sulphates and selenates) series has shown that the system of crystallisation has a preponderating effect on the angular differences, the latter being the smaller the higher the degree of symmetry. It might have been expected, *a priori*, that the monoclinic pair, say, $K_2Mg(SO_4)_2 . 6H_2O$ and $Cs_2Mg(SO_4)_2 . 6H_2O$ would give closer angular values than the more symmetric rhombic pair, for example, K_2SO_4 and Cs_2SO_4, since there is a common "dead weight"; but experience proves the contrary, thus emphasising the effect of difference of system. Now the hexagonal is a higher system in degree of symmetry than the rhombic, and the angular differences (which the author found very small yet clear and unmistakeable in the rhombic sulphates and selenates, although not so large as those shown in the monoclinic double salts) to be expected in the hexagonal system, other factors remaining the same, are still smaller, and might easily fall within the limits 2′–3′ or thereabouts. Jaeger has, in fact, realised such a series, and his results are precisely what the author (Tutton) would have expected. It cannot be emphasised too strongly (*a*) that the author's tables of angles of the whole 31 double sulphates, the 9 double selenates yet investigated, and the whole 10 simple sulphates and selenates, show a general correspondence of mean and calculated values within 2′ for the rhombic simple salts and at most 5′ (probably only 3′) for the monoclinic double salts, and that the constants given by the author for each individual salt can certainly be relied on within these narrow limits; and (*b*) that the deductions made by the author, such as the important one regarding the observed progression with the atomic weight of the alkali metal, are unquestionably valid, since the angular differences in question between the salts under comparison are far and away greater than these small limits of possible error, indeed in the maximum amounting to 2½°.

The author has no doubt of the probable accuracy of the work of Jaeger, the results agreeing perfectly with the author's expectations from the high symmetry displayed. The contribution is, moreover, a very welcome one at the present juncture. But if Jaeger's deduction, as the author understands it, is that literally the axial ratio $a : c$ of his hexagonal salts is rigorously the same for all the salts, the minute differences being considered only chance variations from this mean form, then the author must hold that this view is not a reasonable conclusion, and that it cannot be accepted; it could in any case only be possibly true at some definite temperature. There can be no doubt, however, that each salt has its own particular crystallographic angular values, and that there are real although very minute angular differences between the crystals of the various salts of the series, in accordance with the law of Haüy, which the author (Tutton) considers he has fully substantiated. This law provides that, except when the symmetry imposes identity of crystal angles (as in the cubic system and the 90°, 45°, 60°, and 30° angles of the tetragonal and hexagonal systems), every substance is characterised by its own specific crystalline form, the cases of isomorphism being only close resemblances within the limits of identity of symmetry.

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THE ELECTRICAL CONDUCTIVITY AND LUMINOSITY OF FLAMES CONTAINING SALT VAPOURS.

BY

H. A. WILSON, F.R.S.,
PROFESSOR OF PHYSICS, RICE INSTITUTE, HOUSTON, TEXAS, U.S.A.

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II. *The Electrical Conductivity and Luminosity of Flames containing Salt Vapours.*

By H. A. Wilson, *F.R.S., Professor of Physics, Rice Institute, Houston, Texas, U.S.A.*

Received 31 May,—Read June 17, 1915.

When the vapour of an alkali salt is present in a Bunsen flame the vapour becomes luminous and also increases the electrical conductivity of the flame. The fraction of the salt molecules which are luminous is probably very small, and unless the concentration of the salt vapour is very small the fraction of the salt molecules which are charged electrically, or are ionised, is also very small.

Any particular salt molecule enters the flame at the bottom and moves up the flame with the velocity of the flame gases which is of the order of 200 cm. per second. The molecule is therefore in the flame for only a small fraction of a second, but this time interval is probably long enough for a state of equilibrium to be established between the several states in which the molecules can exist. For example, in the case of sodium chloride there is probably an equilibrium between NaCl, NaOH, Na_2O, Na, H_2O, HCL, and possibly other bodies such as CO, CO_2, and Na_2CO_3.

Each sodium atom must exist in the flame successively in different states and will, on the average, exist in each state a definite fraction of the time it is in the flame. Of course the time interval may not be long enough for every atom to pass through all the possible states, but on the average there will be a definite fraction of all the sodium atoms in each possible state. In some of the possible states the atoms may be luminous during the whole or during only a fraction of the time the atoms are in those states, and during the whole or a part of the time the atoms are in any state they may be positively charged and so form ions. The object of the experiments described in this paper was to obtain information about the relative numbers of the atoms in the different possible states, especially the luminous state and the positively-charged state, and about the nature of the luminous state and the charged state.

In an electric field the charged molecules or ions tend to move with a definite velocity proportional to the electric intensity. This velocity will be denoted by kX, where k is the velocity due to unit field and X the field strength. The average velocity, over a long time, of any particular metal atom due to the field will be fkX, where f denotes the fraction of the time during which the atom is in the positively-charged state. The time during which the atoms are in the flame may not be long enough for each atom to pass through all the possible states, so that actually only a fraction of the atoms may be moved by the field. The average velocity of all the atoms due to the field will be equal to $fk\mathrm{X}$, but only a few atoms may actually move. If this happens, the velocities of those atoms which are moved by the field will lie between zero and $k\mathrm{X}$. A few atoms may be ionised all the time they are in the electric field and these will have the maximum velocity $k\mathrm{X}$.

If the average life of an ion is small compared with the time the molecules are in the electric field, then all the molecules will move with the velocity $fk\mathrm{X}$, but if the average life is not small compared with the time the molecules are in the field, then the velocities will vary between zero and $k\mathrm{X}$, but the average for all the salt molecules will still be equal to $fk\mathrm{X}$.

The rest of this paper is divided into the following sections :—

I. Motion of luminous salt vapours in flames due to an electric field.
II. Velocity of the positive ions of salt vapours in flames.
III. Relation between luminosity and conductivity of salt vapours in flames.
IV. Variation of the conductivity with the concentration of the salt vapour.
V. Relative conductivities due to salts of different metals.
VI. Summary and conclusion.

PART I.—MOTION OF LUMINOUS SALT VAPOURS IN FLAMES DUE TO AN ELECTRIC FIELD.

LENARD[*] found that the luminous streak of vapour from a salt bead in a flame could be deflected towards the negative electrode by a horizontal electric field. This deflexion has since been examined by ANDRADE.[†]

The flame itself is also attracted by the negative electrode. ANDRADE observed the deflexion of the edge of the flame nearest to the negative electrode and subtracted this from the deflexion of the luminous streak to get the deflexion of the streak relatively to the flame gases. He found the deflexion of the flame to be about half that of the streak. I have repeated these experiments and found it difficult to be sure that there was any real difference between the deflexion of the flame and that of the streak of salt vapour. The edge of the flame is not sharply defined, and when salt was put in it seemed to me to change the deflexion of the edge of the flame if the vapour extended to the edge. I also found that in a flame which was little if at all deflected, there was little, if any, deflexion of the salt vapour, although a strong electric field was used.

These preliminary experiments suggested that the deflexion of the luminous streak of salt vapour might be due to the deflexion of the flame as a whole, and not to a relative motion of the luminous salt molecules, through the flame, due to the electric field.

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[*] 'Ann. d. Physik,' 9, 3, pp. 642–650, Oct., 1902.

[†] 'Phil. Mag.,' June, 1912, and July, 1912.

On the other hand, it was found that when the electric field was strong enough to cause a great increase in the current, that is, when an arc discharge began to form, then luminous salt vapour appeared between the streak and the negative electrode; the negative electrode, if in the flame, emitted a stream of luminous salt vapour. The intensity of the luminosity between the streak and the negative electrode was much less than in the streak itself. This suggested that, while the luminous molecules in the streak were not deflected, positive ions were moving out of the streak towards the negative electrode and that these ions could form luminous vapour; these last results are in agreement with some of those of ANDRADE,[*] who showed that positive ions from a streak when deposited on the negative electrode form luminous vapour. This fact was also previously observed by the writer.[†]

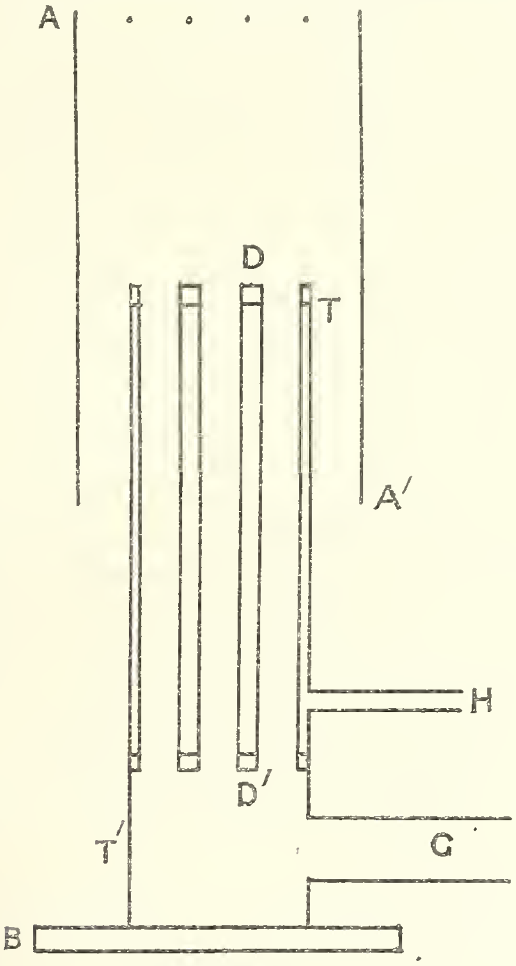

Fig. 1.

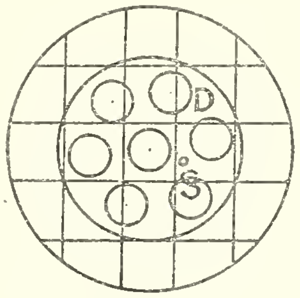

Fig. 2.

It was therefore decided to attempt to measure the relative motion of the luminous salt vapour and flame gases due to an electric field by a new method which seemed to be capable of giving more reliable results than those previously used.

The flame used was a Bunsen flame formed by burning a mixture of gasolene vapour and air from a special burner.

Fig. 1 shows a vertical section of the burner, and fig. 2 the top of it as seen from

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[*] 'Phil. Mag.,' July, 1912.

[†] 'Proc. Royal Institution,' Feb. 12, 1909.

above. A brass tube, TT′, about 3 cm. in diameter and 15 cm. long was soldered to a base plate, B. At D and D′ brass disks were fitted tightly into the tube, TT′. Each of these disks had seven holes bored in it as shown in fig. 2, and seven parallel brass tubes connected the holes in the lower disk, D′, with the holes in the upper disk, D. The mixture of gas and air entered through the side tube, G. The flame had seven sharply defined inner cones. The upper part of the burner was surrounded by a brass tube, AA′, about 4·5 cm. in diameter, supported by three small brass blocks not shown in the figure.

A grating formed of ten platinum wires was fixed across the tube, AA′, about one millimetre from its upper end. This grating was heated bright red hot by the flame and formed one of the electrodes. A mixture of air and spray of a salt solution entered the burner through a second side tube, H, which led into the space between the seven tubes. This mixture entered the flame through a small hole, S, in the upper disk, D, and produced a streak of salt vapour extending from S to the top of the flame. The air and spray entered H through a stop-cock which was rapidly opened and closed by means of an electric motor. The streak of vapour was therefore not continuous, but consisted of a series of puffs of vapour moving up the flame. The amount of salt in each puff could be varied by adjusting the pressure of the supply of air and spray. It could be diminished till the puffs were only just visible or increased till they were intensely luminous.

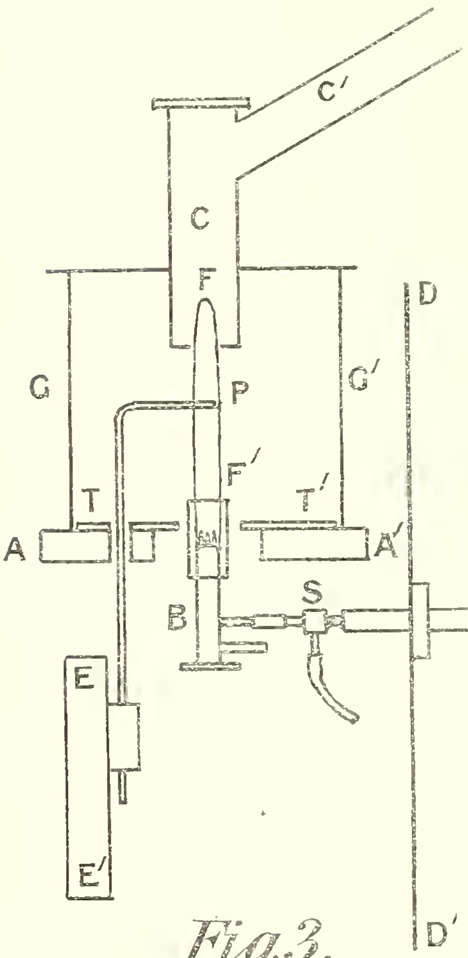

Fig.3.

The shaft of the motor carried a disk having four equidistant openings near its circumference. The stop-cock was opened four times during each revolution of the motor. The flame could be observed through the rotating disk so that it was then seen as many times per second as the stop-cock was opened. The puffs of salt vapour were then seen in the flame apparently stationary in a series of nearly equidistant positions one above the other. Fig. 3 shows the apparatus used. B is the burner and FF′ the flame. S is the stop-cock through which the air and spray entered, and DD′ the rotating disk carried by the motor shaft, M. AA′ is a wooden base covered with a sheet of asbestos, TT′. GG′ is a glass cylinder resting on the wooden base. The top of the cylinder is covered by a brass plate in the centre of which is fixed a vertical brass tube, C, which, with a tube, C′, formed a chimney up which the gases from the flame were led out of the room. The lower end of the tube, C, was fitted with a brass disk having a hole in it about 4 cm. in diameter, which was covered with a platinum wire grating like the one above the burner, B. At P a fine platinum wire was stretched horizontally across the flame perpendicular to the plane of the paper. This wire was carried by a glass tube which was supported on a slide, EE′, so that the wire could be moved up and down along the vertical axis of the flame. The slide was provided with a millimetre scale and vernier. The potential difference between the wire, P, and the burner grating could be measured with an electrostatic voltmeter.

The tube, C, and the upper grating were usually connected to the earth, through a galvanometer, and the burner, B, and lower grating could be connected to a battery of 1800 dry cells, giving up to 2700 volts. In this way a vertical electric field could be maintained in the flame between the upper and lower gratings.

Let v denote the upward velocity of the flame, n the number of puffs of salt entering the flame per second, x_1 the height of a puff as seen through the rotating disk and x_2 the height of the next puff higher up. In the absence of an electric field the puffs simply move up with the flame so that

$$v = n(x_2 - x_1).$$

The heights of the puffs could be measured by adjusting the wire, P, so that it coincided with their tops or bottoms and reading the vernier on the slide, EE′. About three puffs were visible when the number of puffs was rather over 100 per second.

The puffs were equidistant showing the velocity of the flame to be sensibly uniform. It was found that $x_2 - x_1$ was nearly 3 cm. when N was equal to 100 per second. The velocity of the flame was therefore about 300 cm. per second and could be determined to within two or three per cent. without difficulty. The gas and air supplies to the flame were carefully regulated, and the gas and air were well mixed before they entered the burner. The burner gave an exceptionally steady and only slightly conical flame in the space between the wire gratings.

Let k denote the velocity of a luminous salt molecule in the flame due to an electric field of unit strength. We have

$$dx' = (v - k\mathrm{X})\, dt,$$

where x' denotes the height of the molecule above the lower grating, X the electric force reckoned positive when directed downwards, and t the time. Also in the absence of an electric field let

$$dx = v\, dt,$$

where x denotes the height of the molecule in this case.

Hence

$$dx - dx' = \frac{k}{v} \mathrm{X}\, dx,$$

which gives

$$x - x' = \frac{k}{v} \int_0^x \mathrm{X}\, dx.$$

But $\int_0^x \mathrm{X}\, dx$ denotes the potential difference between the lower grating and the point a distance x higher up. Let this potential difference be denoted by V so that

$$k = v\,(x - x')/\mathrm{V}.$$

Here $x - x'$ is the distance through which a puff of salt appears to be moved downwards, as seen through the rotating disk, when the lower grating is connected to the battery.

Since $v = n\,(x_2 - x_1)$ we have

$$k = \frac{n\,(x_2 - x_1)\,(x - x')}{\mathrm{V}}.$$

If the puffs contain much salt vapour they have a greater conductivity than the rest of the flame so that the electric field will be less in the puffs than in the rest of the flame. In this case the salt inside the puffs will not be acted on by the whole of the potential fall, V, so that the deflexion of the puffs will be smaller than that represented by the equation just given. In the case of sodium and strontium salts, which have small conductivity and intense luminosity, it was possible to observe the puffs when the amount of salt in them was not enough to change the conductivity appreciably so that with these salts no error could be produced by the conductivity of the puffs. The fact that the conductivity with small amounts of these salts was not appreciable was shown by measuring the current with the stop-cock open all the time so as to get a continuous streak of the salt vapour. With small amounts of the salts the current was not increased by the salt more than 50 per cent. With the apparatus described it was found that the puffs of salt vapour did not appear to move at all when the battery was connected or disconnected. A motion of 0·5 mm. could have been detected, and V was increased to over 2000 volts in the case of some salts. This shows that k was less than

$$\frac{100 \times 3 \times 0\cdot05}{2000} = 0\cdot0075 \text{ cm. per second per volt per centimetre.}$$

Salts of sodium, strontium and potassium were tried and no deflexion of the puffs of vapour could be detected in any case. The amount of salt in the puffs was varied as much as possible in each case. With sodium and strontium V was increased to over 2000 volts, but with potassium it could not be raised above about 1000 volts without an arc striking between the electrodes. With sodium and strontium in small amounts and large potentials the fall of potential was nearly uniform, but with potassium it nearly all occurred near the lower negative electrode.

It was found that if the tube, AA′ (fig. 1), carrying the lower grating was removed and the burner itself used as the lower electrode then the puffs of salt were deflected downwards when the burner was charged negatively. The deflexion was about 0·5 cm. for 1000 volts in the case of all salts.

This gives

$$k = \frac{100 \times 3 \times 0{\cdot}5}{1000} = 0{\cdot}15 \text{ cm. per second per volt per centimetre.}$$

Charging the burner negatively when the tube, AA′, was removed depressed the inner cones of the flame and caused the flame to broaden out slightly just above the burner. Evidently the electric field retarded the upward motion of the flame and so produced the downward deflexion of the puffs of salt vapour. When the burner was charged positively no deflexion could be detected. The tube, AA′, and platinum grating were therefore used to shield the inner cones from the electric field and to allow the puffs of salt to get well mixed with the flame before entering the field. The tube, AA′, also served to greatly steady the flame. The flame is not affected by the field when the tube, AA′, and lower grating are used because it is practically uniform throughout the distance between the upper and lower gratings.

Since no deflexion of the puffs was obtained when using the lower grating and the tube, AA′, it appears that the luminous salt vapours in flames do not really move relatively to the flame in an electric field. I think the motion observed by LENARD, EBERT and ANDRADE was due to the deflexion of the flame which is difficult to estimate and allow for.

ANDRADE found $k = 0{\cdot}16$ cm. per second per volt per centimetre, which is about twenty times the upper limit given by the experiments just described, but agrees nearly with the value found when the lower part of the flame was not protected from the electric field. When the potential difference between the two gratings was increased sufficiently an arc formed accompanied by a great increase in the current. The arc could be seen to form a luminous streak down the flame, and the electrodes got very hot at each end of the arc and fused if the arc was allowed to continue for long. When an arc was formed the puffs of salt vapour became more brightly luminous and the coloration due to the salt could be seen, although faintly, all along the track of the arc. The position of the puffs was not changed when an arc formed. It appears, therefore, that positive ions move down the flame from the puffs when an arc is formed and form a small amount of luminous salt vapour in the arc. I think some positive ions are probably deflected downwards from the puffs, even when the field is not strong enough to arc, but they are not numerous enough to form visible vapour. In the arc the temperature is higher so that a smaller amount of salt vapour becomes perceptibly luminous.

Part II.—Velocity of the Positive Ions of Salt Vapours in Flames.

Some new experiments on the velocity of the positive ions of salt vapours in flames will now be described.

The apparatus of the previous section with some modifications was used. The central part of the grating at the top of the tube, AA′ (fig. 1), was removed and an insulated platinum wire electrode supported in the gap, so that the grating formed a guard ring round it. The wire supporting this electrode passed through a hole in the tube, AA′, about 3 cm. from the top of it. This electrode was connected to a galvanometer, the other terminal of which was connected to the burner, B. The arrangement is shown in fig. 4. The upper grating electrode was connected to earth and the burner, B, was charged negatively. The galvanometer then indicated a small current passing down the flame from the upper grating to the electrode in the middle of the lower grating. Most of the current through the flame went to the guard ring and so was not indicated by the galvanometer. The potential gradient in the flame could be measured with the wire, PP′, as before. The velocity of the flame was found with the puffs of salt vapour, but the puffs were not sent into the flame except when its velocity was being measured.

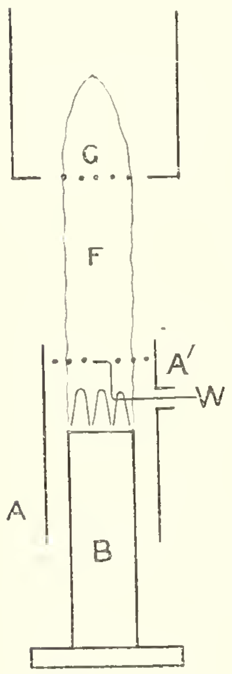

Fig. 4.

F, flame.
B, burner.
AA′, tube round burner.
G, upper grating.
W, wire electrode.

A bead of salt on a platinum wire could be introduced into the flame just below the upper grating, and the effect of the bead on the current through the galvanometer and on the potential gradient was determined. The distance between the upper and the lower gratings was about 7 cm.

It was found that putting in beads of lithium, sodium, potassium, rubidium, cæsium and strontium salts had no appreciable effect on the current or on the potential gradient below the bead with any potential difference from zero to 2700 volts. The potential gradient just below the bead was about 100 volts per centimetre when the P.D. used was 2700 volts. The velocity of the flame was 300 cm. per second. This shows that the positive ions from the beads did not move down the flame, even with the P.D. of 2700 volts, so that their velocities due to 1 volt per centimetre were less than 3 cm. per second.

The distance between the upper and lower gratings was then reduced to about 3 cm. It was then found that putting in a bead of any salt just below the upper electrode slightly increased the current and also slightly increased the potential gradient below the salt. The gradient in the salt vapour above the bead was very small, so that, since the salt vapour occupied about 1 cm. of the flame below the upper electrode, the effect of the salt was much the same as moving the electrodes 1 cm.

nearer together. The increase in the current was about 25 per cent. with potentials up to 1800 volts. With 2700 volts the increase was larger, varying from 50 to 300 per cent. with different salts. This indicates that between 1800 and 2700 volts the positive ions began to move down the flame. If the salt beads were put into the flame about 1 cm. or 2 cm. below the upper grating, instead of close to it, an arc started with 2700 volts. Luminous salt vapour could be seen along the whole length of the arc.

The potential gradient below the beads of salt with potentials between 1800 and 2700 volts was about 300 volts per centimetre. Since the velocity of the flame was 300 cm. per second, this shows that the velocity of the positive ions was about 1 cm. per second for one volt per centimetre. The velocity was about the same for all salts, but could not be estimated accurately because the changes in the current due to putting in the beads increased gradually with the potential difference. It appears that the maximum velocity of the positive salt ions due to 1 volt per centimetre is not much greater than 1 cm. per second.

In the earlier experiments by the writer,[*] it was found that a bead of salt below the upper electrode began to increase the current at a P.D. of about 100 volts. LUSBY[†] obtained a similar result and also found that the salt diminished the potential gradient below the bead. These results appear to have been due to a small amount of salt getting into the flame below the bead. This was prevented, in the experiments just described, by the chimney attached to the upper electrode. In the absence of the chimney, it was found that putting a bead below the upper electrode increased the current and diminished the potential gradient even with small potential differences. The salt vapour from the bead gets into the lower parts of the flame partly by circulating round with the air surrounding the flame inside the apparatus and partly by escaping into the air in the room and then entering the burner along with the air supply. The chimney entirely stopped both these processes. There was a strong draught up the chimney so that the salt vapour from the bead went straight up the chimney and did not get into the air surrounding the flame.

It appears that the earlier attempts to measure the velocity of the positive ions of salt vapours in flames gave values much too high. ANDRADE[‡] has recently obtained values of about 3 cm. per second for 1 volt per centimetre for the positive ions of strontium salts. The difference between this and the value of about 1 cm. per second just obtained may be due partly to differences between ANDRADE's flames and mine. Also there may have been a few positive ions, even in my flames, with velocities greater than 1 cm. per second.

When a large increase in the current is produced by putting in the bead an arc forms as already mentioned. The potential gradient necessary to start an arc was

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[*] 'Phil. Trans.,' A, vol. 192, p. 499, 1899.

[†] 'Proc. Camb. Phil. Soc.,' vol. xvi., Pl. 1, 1910.

[‡] *Loc. cit.*

rather greater than 300 volts per centimetre. I think, when any great number of positive ions moves down to the negative electrode an arc starts because the positive ions form salt vapour by recombining with negative ions, and the salt diminishes the drop of potential at the negative electrode and so increases the gradient between the electrodes. The gradient required for an arc to start on putting in a bead of salt is, therefore, probably that required to make a large number of positive salt ions move down the flame. According to the earlier experiments all salts give positive ions having equal velocities. This conclusion is probably correct in spite of the large error made in the absolute value of the velocity. The salt vapour really extended down the flame nearly to the lower electrode and was not confined to the part of the flame close to the bead as was supposed. The potential gradient which made the ions move down was therefore the gradient just above the lower electrode and not that just below the bead. This explanation of the large velocities obtained in the earlier experiments was suggested by ANDRADE. The present experiments have convinced me that his suggestion is correct.

PART III.—RELATION BETWEEN LUMINOSITY AND CONDUCTIVITY OF SALT VAPOURS IN FLAMES.

Some experiments on the changes in the luminosity and conductivity of flames containing sodium chloride, due to the addition of chloroform, will now be described.

A mixture of air, spray of a sodium chloride solution and gasoline vapour produced by a sprayer was passed through a T-tube into two similar burners. The tube to one of the burners led the mixture through a vessel in which chloroform could be placed.

The luminosities of the two flames were compared by means of a Hilgers' spectrophotometer.

Each flame contained two platinum electrodes separated by a horizontal distance of about 8 cm. A current from a battery of from 10 to 300 cells could be passed between these electrodes. In each flame two fine platinum wires were introduced about 5 cm. apart, and either pair could be connected to a quadrant electrometer. These wires were horizontal and perpendicular to the horizontal line joining the centres of the electrodes between which the current was passed.

The current between the electrodes was measured with a galvanometer, and the ratio of the current to the potential difference between the fine wires was taken as a measure of the conductivity. When no chloroform was used the two flames had equal conductivities and luminosities.

The following table contains the results obtained :—

Solution in sprayer (grammes NaCl per litre).	Ratio of conductivities (without $CHCl_3$ ÷ with $CHCl_3$).	Ratio of luminosities (without $CHCl_3$ ÷ with $CHCl_3$).
0	8·0	1·9
0·8	5·7	2·1
4	6·0	1·9
20	6·1	1·9
200	6·0	1·9

It appears that for all concentrations of the sodium chloride the chloroform diminished the conductivity about six times, and the luminosity about two times.

It was found that the chloroform increased the current through the flame, although it diminished the conductivity. The current depends on the conductivity throughout the volume of the flame and on the resistance close to the negative electrode. The flame, away from the negative electrode, obeys OHM's law, but at the negative electrode there is a large fall of potential which is approximately proportional to the square of the current. The chloroform increased the current from four to ten times. Since the conductivity, measured by the ratio of the current to the potential gradient between the two wires, was diminished, it follows that the chloroform must have considerably diminished the fall of potential at the negative electrode.

If potassium carbonate is put on the negative electrode the fall of potential there almost disappears, and then the current depends on the conductivity of the rest of the flame. It was found that with potassium carbonate on the negative electrode the chloroform decreased the current about six times in agreement with the change in the conductivity. The effect of the chloroform on the temperature of the flame was measured with a thermocouple. It was found that the temperature of the couple was changed from about 1650° C. to 1600° C.

If the current through the flame had been taken as a measure of its conductivity a large increase in the conductivity accompanied by a diminution of the luminosity would have been found.

The relation between the potential difference used to send a current through a flame between clean platinum electrodes and the current is represented by the equation

$$V = Acd + Bc^2.$$

Where V denotes the P.D., c the current, d the distance between the electrodes, and A and B are constants. The term Bc^2 represents the fall of the potential at the negative electrode, and the term Acd the fall of potential in the uniform gradient between the electrodes. It appears that the chloroform diminishes B but increases A.

With small potentials and currents the term Acd is relatively more important, so that the chloroform then should decrease the current, while with large potentials the term Acd becomes negligible and then the chloroform increases the current.

In the experiments of SMITHELLS, DAWSON, and the writer[*] it was found that chloroform diminished the current with very small potentials but increased it with larger potentials. The potentials used in the present experiments were large and the chloroform increased the current.

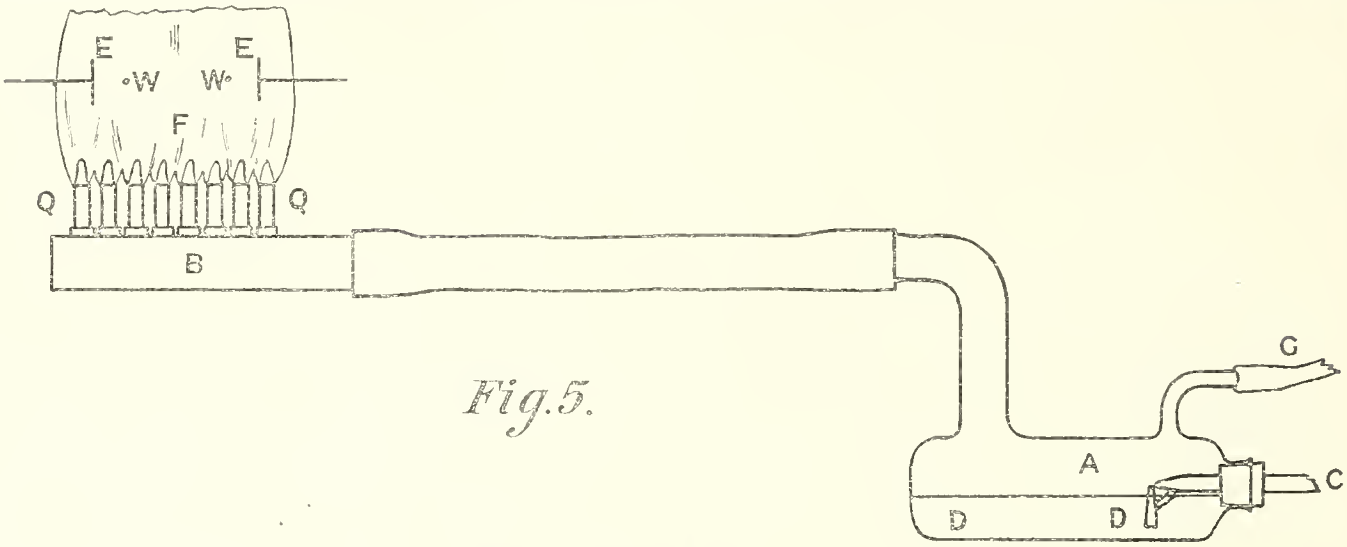

Fig. 5.

B, burner.
F, flame.
EE, electrodes.
WW, platinum wires.
A, sprayer.
DD, salt solution.
G, gas inlet.
C, air inlet.
QQ, row of quartz tubes.

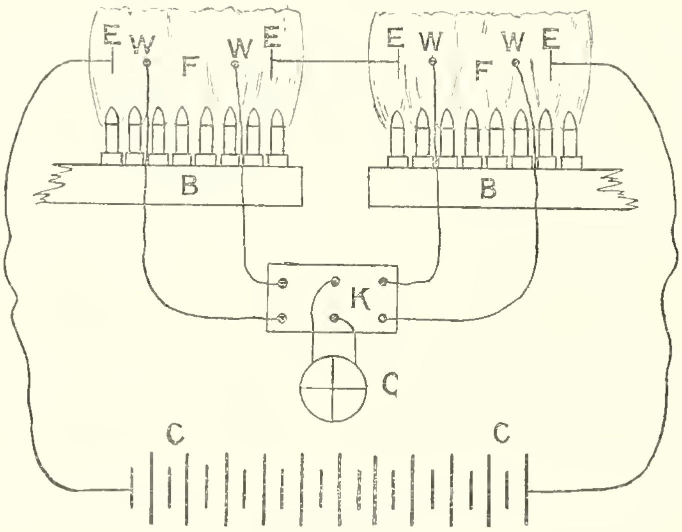

Fig. 6.

BB, burners.
FF, flames.
EEEE, electrodes.
WWWW, platinum wires.
K, commutator.
Q, quadrant electrometer.
CC, battery.

It is clear that the current is not a measure of the conductivity, but the ratio of the current to the uniform electric intensity away from the negative electrode is proportional to the true conductivity of the flame.

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[*] 'Phil. Trans.,' A, vol. 193, p. 89, 1899.

Experiments on the variation of the conductivity and luminosity with the concentration of the salt vapour in the flame will now be described. Two similar and equal sprayers were used, supplying a mixture of air, gas and spray, to two equal burners. The sprayers were adjusted so that when both contained the same solution the two flames had equal conductivities and luminosities. The electrodes in the two flames were connected in series so that the same current passed through each flame. The uniform potential gradients in the flames were then inversely proportional to their conductivities. Fig. 5 shows one of the burners and its sprayer. Fig. 6 shows the two flames and the electrical connections. The luminosities were compared with the spectrophotometer.

The following table contains the results obtained with solutions of sodium chloride :—

Solutions sprayed (grammes NaCl per litre).		Ratio of conductivities.	Ratio of luminosities.
Flame A.	Flame B.	A/B.	A/B.
20	20	1·00	1·00
20	4	2·21	2·14
20	0·8	5·00	4·62
20	0·16	9·00	9·75
20	0	33·3	36·7
4	0·8	2·26	2·16
0·8	0·16	2·40	2·11
0·16	0·032	1·70	2·90

It appears that both the luminosity and conductivity are roughly proportional to the square root of the concentration of the sodium chloride in the flame. It was shown by GOUY[*] that the luminosity is nearly proportional to the square root of the concentration.

The following results were obtained with sodium carbonate solutions :—

Solutions sprayed (grammes Na_2CO_3 per litre).		Conductivities.	Luminosities.
Flame A.	Flame B.	A/B.	A/B.
18·12	18·12	1	1
18·12	1·812	3·1	2·9
18·12	0·1812	9·8	8·6

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[*] 'Ann. Chim. et Phys.,' (5), 18, pp. 5–101 (1879).

It appears that the conductivity and luminosity due to the sodium carbonate are nearly proportional to the square root of the concentration as with sodium chloride.

The following results were obtained:—

Solutions sprayed (grammes per litre).		Conductivities.	Luminosities.
Flame A. NaCl.	Flame B. Na_2CO_3.	A/B.	A/B.
200	181·2	1·00	1·00
20	18·12	1·00	1·00
2	1·812	1·00	1·00
0·2	0·1812	1·00	1·00

It appears that the conductivities and luminosities of sodium chloride and sodium carbonate in any chemically equivalent quantities are equal.

The luminosity due to a sodium chloride solution containing 20 gr. per litre was found to be equal to that due to a solution containing 20 gr. of sodium chloride and 200 c.c. of strong hydrochloric acid per litre. Thus an excess of HCl does not affect the luminosity due to NaCl. This agrees with the conclusion that the effect of $CHCl_3$ on the luminosity due to NaCl is due to the change in the character of the flame and not to chemical action.

It was found that the sodium light luminosity due to a solution containing 18·12 gr. Na_2CO_3 per litre was equal to that due to a solution containing 18·12 gr. Na_2CO_3, and 23·6 gr. K_2CO_3 per litre. The conductivity due to the solution containing K_2CO_3 was about nine times that due to the one containing only Na_2CO_3. The negative ions from the K_2CO_3 must have diminished the number of positive sodium ions nine times, so that this result agrees with the conclusion that sodium light is not due to positive ions.

PART IV.—THE RELATION BETWEEN THE CONDUCTIVITY AND THE CONCENTRATION OF SALT VAPOURS IN FLAMES.

The earlier experiments of ARRHENIUS[*] and of SMITHELLS, DAWSON and the writer[†] showed that the current is nearly proportional to the square root of the concentration when the concentration is small. SMITHELLS, DAWSON and the writer found that with larger concentrations the current due to oxysalts increases much more rapidly than as the square root of the concentration. In all these earlier

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[*] 'Wied. Ann.,' vol. xliii., p. 18, 1891.

[†] 'Phil. Trans.,' A, vol. 193, p. 89, 1899.

experiments the current, due to a constant P.D., between two platinum electrodes near together in the flame, was taken as a measure of the conductivity.

The relation $V = Acd + Bc^2$ shows that when the electrodes are near together and the term Acd therefore small, the current depends mainly on the fall of potential at the negative electrode which is represented by Bc^2.

The conductivity of the flame in the uniform potential gradient between the electrodes has little influence on the current when the electrodes are near together.

It seemed likely that measurements of the conductivity, as measured by the ratio of the current to the uniform potential gradient, away from the negative electrode, might give simpler and more easily interpreted results than those previously obtained.

The apparatus described in the preceding section of this paper was used. The same current was passed through two similar flames and the ratio of the uniform potential gradients in them measured. The amount of salt in one flame was kept constant and that in the other varied. In this way the ratios of the conductivities of the second flame, with different amounts of salt in it, were found. The first flame merely served as a standard with which to compare the second one. It was not assumed that the two flames had equal conductivities when solutions of equal strength were sprayed into them, although this was roughly true. Variations in the gas and air supplies probably affected both flames nearly equally, and therefore had little effect on the results obtained.

The following results were obtained with solutions of cæsium chloride :—

Solutions sprayed (grammes CsCl per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
20·2 (RbCl)	80	3·13
20·2 (RbCl)	8	1·00
20·2 (RbCl)	0·8	0·301
0·08	0·016	0·535
0·08	0·032	0·813
0·08	0·08	1·37
0·08	0·16	1·92
0	0	1·00
0	0·0032	2·88
0	0·008	5·72
0	0·016	8·90
0·8	0·8	0·75
0·8	0·08	0·21

The following tables gives the conductivities of the flame containing different amounts of CsCl, deduced from the above results, taking that of the flame without salt equal to unity :—

Solution sprayed (grammes CsCl per litre).	Conductivity.
0	1
0·0032	2·88
0·008	5·72
0·016	8·9
0·032	13·5
0·08	22·7
0·16	32·8
0·8	85·2
8·0	282
80	883

The ionic theory of the variation of the conductivity with the concentration will now be considered.

Let S denote the number of salt molecules per cubic centimetre in the flame, ionised or not, and n the number of positive salt ions per cubic centimetre. Then $S-n$ will be the number of non-ionised salt molecules if we suppose one salt molecule gives one positive ion.

Let F denote the number of flame molecules per cubic centimetre, which can be ionised, and m the number of flame-positive ions per cubic centimetre, $F-m$ is then the number of non-ionised flame molecules per cubic centimetre.

We then have

$$S-n = \alpha n(n+m). \qquad (1)$$

$$F-m = \beta m(n+m), \qquad (2)$$

where α and β are constants; α is the ratio of the coefficient of recombination of the positive salt ions with the negative ions to the fraction of the non-ionised salt molecules which ionise per second; β is the same thing for the flame-positive ions. F is very large compared with S, and m is usually small compared with n. Hence m must be extremely small compared with F, so that $F-m$ may be replaced by F.

The conductivity (c) of the flame is proportional to the total number of ions per cubic centimetre, so that

$$Ac = n+m, \qquad (3)$$

where A is a constant.

Replacing $F-m$ by F and eliminating n and m from (1), (2), and (3), we obtain

$$\frac{S}{1+\alpha Ac}+\frac{F}{\beta Ac}=Ac.$$

If we take $c=1$ when $S=0$ this becomes

$$\frac{S}{1+\alpha Ac}=Ac-\frac{A}{c}$$

or

$$S=A\frac{c^2-1}{c}(1+\alpha Ac). \qquad (4)$$

When c is large this reduces to

$$S=\alpha A^2c^2.$$

Since all salts give ions having the same velocities in the flame, it follows that the constant A should have the same value for all salts. The equation (4), therefore, only contains one constant (α) which varies with the nature of the salt.

The fraction of the salt molecules which are ionised is given by

$$\frac{n}{S}=\frac{1}{1+\alpha Ac}.$$

Let k denote the concentration in grammes per litre of the solution sprayed into the flame, and let $GS=10^4k$, where G is a constant proportional to the molecular weight of the salt.

We have then

$$10^4k=GA\left\{\frac{c^2-1}{c}\right\}(1+\alpha Ac).$$

When c is large suppose $10^4k=ac^2$, so that $a=G\alpha A^2$, and let $b=GA$, so that

$$10^4k=\frac{c^2-1}{c}(b+ac). \qquad (5)$$

and

$$\frac{n}{S}=\frac{b}{b+ac}. \qquad (6)$$

The equation (5) agrees with the values of c found for cæsium chloride within the limits of experimental error if $b=10$ and $a=1$. The following table gives the values of 10^4k calculated from (5), using the observed values of c. The calculations were done with a slide rule :—

c.	k (calculated).	k (experimental).
1	0	0
2·88	0·00326	0·0032
5·72	0·0087	0·008
8·9	0·0166	0·016
13·5	0·0315	0·032
22·7	0·074	0·08
32·8	0·14	0·16
85·2	0·81	0·8
282	8·2	8·0
883	79·0	80·0

The experimental numbers for c are probably reliable to about 5 per cent., so that when k is calculated from c the results may be in error by 10 per cent.

The calculated and experimental values of k agree to less than 10 per cent. in nearly all cases. When the enormous variation in k, from 0·0032 to 80, is taken into account, it may be said that the results are in good agreement with the ionic theory.

Since

$$\frac{n}{S}=\frac{b}{b+ac},$$

we get for cæsium chloride

$$\frac{n}{S}=\frac{10}{10+c}.$$

The following table gives the percentage of the CsCl molecules, which are ionised in the flame according to this equation :—

Solution sprayed (grammes CsCl per litre).	$\frac{n}{S}\times 100$.
0	90·9
0·0032	75·6
0·032	41·8
0·16	22·0
0·8	10·6
8·0	3·5
80·0	1·1

The salt vapour is not completely ionised when its concentration is extremely small, because of the finite number of flame ions present with which the salt ions can recombine.

PART V.—THE RELATIVE CONDUCTIVITIES OF SALTS OF DIFFERENT ALKALI METALS.

The relative conductivities of salts of different metals were determined with the apparatus described in Section III. The two flames were adjusted so that they had equal conductivities when the same solution was sprayed into them.

It was found that when the concentrations were large the conductivity was nearly proportional to the square root of the concentration with all salts. Results proving this to be true will be given later in this section. It follows that the ratio of the conductivities of any two salts, at equal concentrations, is independent of the concentration provided the concentration is large.

The following table gives the results obtained :—

Solutions sprayed (grammes per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
18·12 Na_2CO_3	23·6 K_2CO_3	9·3
18·12 Na_2CO_3	25·6 KCl	9·3
25·6 KCl	20·2 RbCl	0·89
8 CsCl	20·2 RbCl	0·89

The following table gives the relative conductivities, at large concentrations, of the salts of different metals for concentrations such that equal numbers of metal atoms are present in the flame in each case. The conductivity for sodium salts is taken equal to unity :—

Salt.	Relative conductivities.
NaCl	1
Na_2CO_3	1
KCl	9·3
K_2CO_3	9·3
RbCl	11·8
CsCl	25·02

These numbers were calculated from the relative conductivities given in the previous table. It was shown in Section III. that NaCl and Na_2CO_3 have equal conductivities when present in chemically equivalent amounts.

The following table gives the relative concentrations (proportional to metal atoms per unit volume) for which the conductivities are equal. These numbers are also only correct for large concentrations. The concentration is taken as unity in the case of cæsium:—

Metal.	Atomic weight.	Concentration.
Na	23	626·0
K	39	7·25
Rb	85	4·48
Cs	133	1·00

The equation $10^4 k = \frac{c^2-1}{c}(b+ac)$, which was found to represent the results obtained with cæsium chloride, can be applied to the other salts also.

The constant a is proportional to the large concentrations in grammes per litre which give equal conductivities. The constant b has the same value for all salts when the concentrations are taken proportional to the number of metal atoms in unit volume. When the concentrations are expressed in grammes per litre b is proportional to the molecular weight of the salt actually present in the flame. Since chlorides and carbonates give equal conductivities it is probable that chemically equivalent amounts give equal numbers of salt molecules in the flame. Probably the carbonates and chlorides are decomposed into oxides. The constant b for alkaline carbonates is therefore probably proportional to one-half their molecular weights.

The following table gives the values of a and b calculated in this way so as to give k in grammes per litre in the solution sprayed into the flame:—

Salt.	a.	b.
NaCl	217·00	3·47
Na_2CO_3	197·00	3·14
KCl	3·20	4·42
K_2CO_3	3·0	4·10
RbCl	3·20	7·20
CsCl	1·00	10·00

The following is an example of the method used for calculating the above constants. For RbCl we have

$$a = 1 \times 4{\cdot}48 \times \frac{121}{168{\cdot}5} = 3{\cdot}2.$$

Here 1 is the value of a for cæsium chloride, 4·48 is the equivalent large concentration at which rubidium salts have conductivities equal to cæsium salts at the large concentration unity, 121 is the equivalent weight of RbCl, and 168·5 that of CsCl. Also for RbCl

$$b = 10 \times \frac{121}{168 \cdot 5} = 7 \cdot 20$$

where 10 is the value of b found for CsCl.

To see if the equation $10^4 k = \frac{c^2-1}{c}(b+ac)$ would give results agreeing with experimental values, using the values of a and b given above, a number of measurements of the relative conductivities at small concentrations were made.

The following results were obtained with solutions of RbCl:—

Solutions sprayed (grammes RbCl per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
0·0202	0	0·178
0·0202	0·00202	0·34
0·0202	0·0202	1·30
0·0202	0·202	4·32

Taking the conductivity when spraying water equal to unity, these results give the following numbers:—

Solution sprayed (grammes RbCl per litre) (k).	Conductivity (found).	k (calculated).
0	1	0
0·00202	1·91	0·0019
0·0202	7·30	0·0219
0·202	24·2	0·202

The last column contains the values of k given by the equation

$$10^4 k = \frac{c^2-1}{c}(7 \cdot 2 + 3 \cdot 2c).$$

The following results were obtained with potassium carbonate :—

Solution sprayed (grammes K_2CO_3 per litre).		Ratio of conductivities.
Flame A.	Flame B.	B/A.
0·0236	0	0·164
0·0236	0·00236	0·338
0·0236	0·0236	1·300
0·0236	0·236	4·59
2·36	0·236	4·61
2·36	2·36	1·39

Taking $C = 1$ when $k = 0$, these results give the following values :—

Solution sprayed (grammes K_2CO_3 per litre) (k).	Conductivity (found).	k (calculated).
0	1	—
0·00236	2·07	0·00164
0·0236	7·98	0·0221
0·236	28·0	0·246
2·36	84·6	2·18

The numbers in the third column are those given by the equation

$$10^4 k = \frac{c^2-1}{c}(4{\cdot}1+3c).$$

In Section III. the relative conductivities of several sodium chloride solutions are given. The following table gives numbers calculated from those results taking $c = 30{\cdot}3$ when $k = 20$ gr. per litre. The value $c = 30{\cdot}3$ when $k = 20$ was got from the relative conductivities found for cæsium and sodium salts :—

Solution sprayed (grammes NaCl per litre) (k).	Conductivity (found).	k (calculated).
20	30·3	19·9
4	13·7	4·05
0·8	6·06	0·79
0·16	2·95	0·168
0·032	1·73	0·044

The last column contains numbers given by the equation $10^4k = \frac{c^2-1}{c}(3{\cdot}5+217c)$.

The following table gives the percentage of the salt molecules ionised when k is very small so that $c = 1$. These numbers were calculated by means of the equation

$$\frac{n}{S} = \frac{b}{b+ac},$$

putting $c = 1$.

Salt.	$\frac{n}{S} \times 100$.
NaCl	1·6
Na_2CO_3	1·6
KCl	58·0
K_2CO_3	58·0
RbCl	69·0
CsCl	90·9

The ionization is not complete when the concentration of the salt vapour is very small because of the finite number of flame ions present with which the salt ions can recombine.

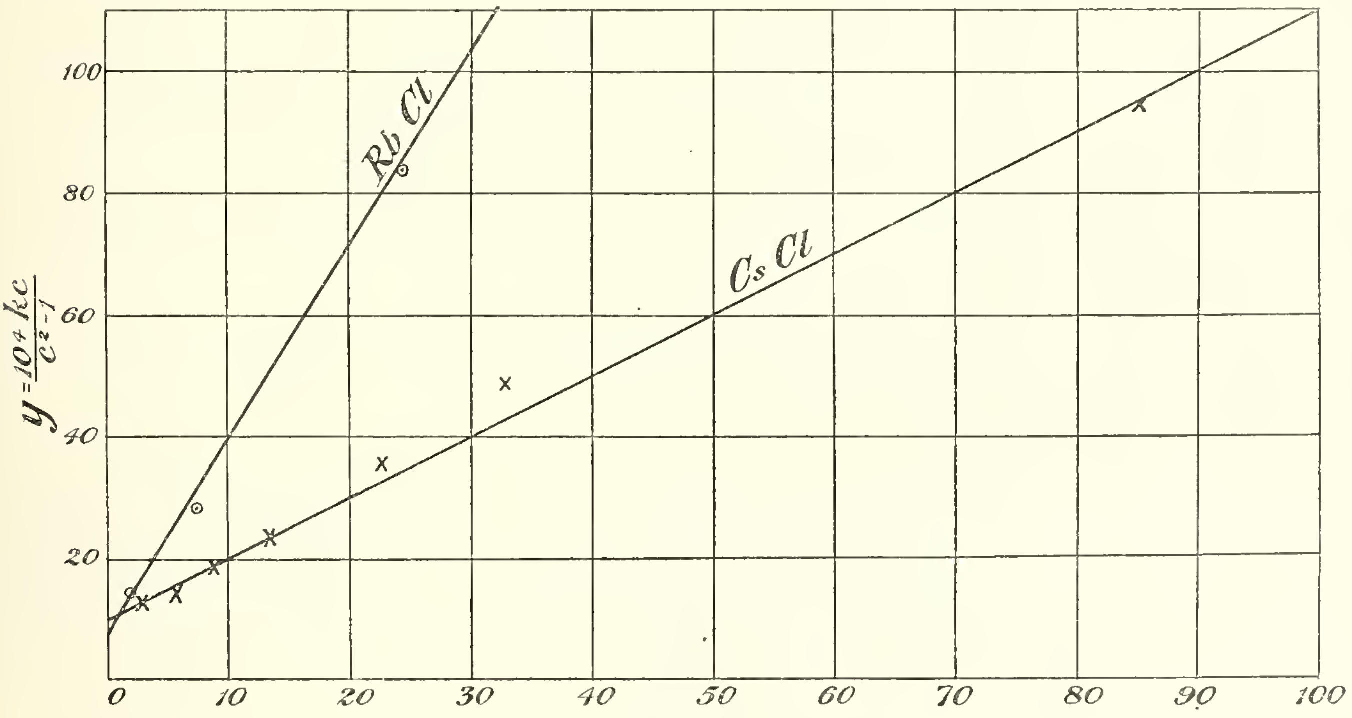

Fig 7

The equation $10^4k = \frac{c^2-1}{c}(b+ac)$ shows that $\frac{10^4kc}{c^2-1}$ is a linear function of c. Fig. 7 shows graphically the relation between the experimental values of $\frac{10^4kc}{c^2-1}$ and c for

CsCl and RbCl. The straight lines are those given by the equation $y = b+ac$. The crosses representing the experimental results fall nearly on the straight lines. Fig. 8 and fig. 9 show the same thing for K_2CO_3 and NaCl. In the case of NaCl the straight line passes practically through the origin but with the other salts it is clear that this is not the case. The larger values of c and $\frac{10^4kc}{c^2-1}$ are not shown. They were used to calculate the constant a and so, of course, the points representing them would fall on the straight lines given by $y = b+ac$ since b becomes negligible when c is large.

If a solution containing two or more salts is sprayed into the flame, then, since the ions from one salt can combine with the ions from the other, the conductivity should not be equal to the sum of the conductivities due to equal amounts of each salt alone.

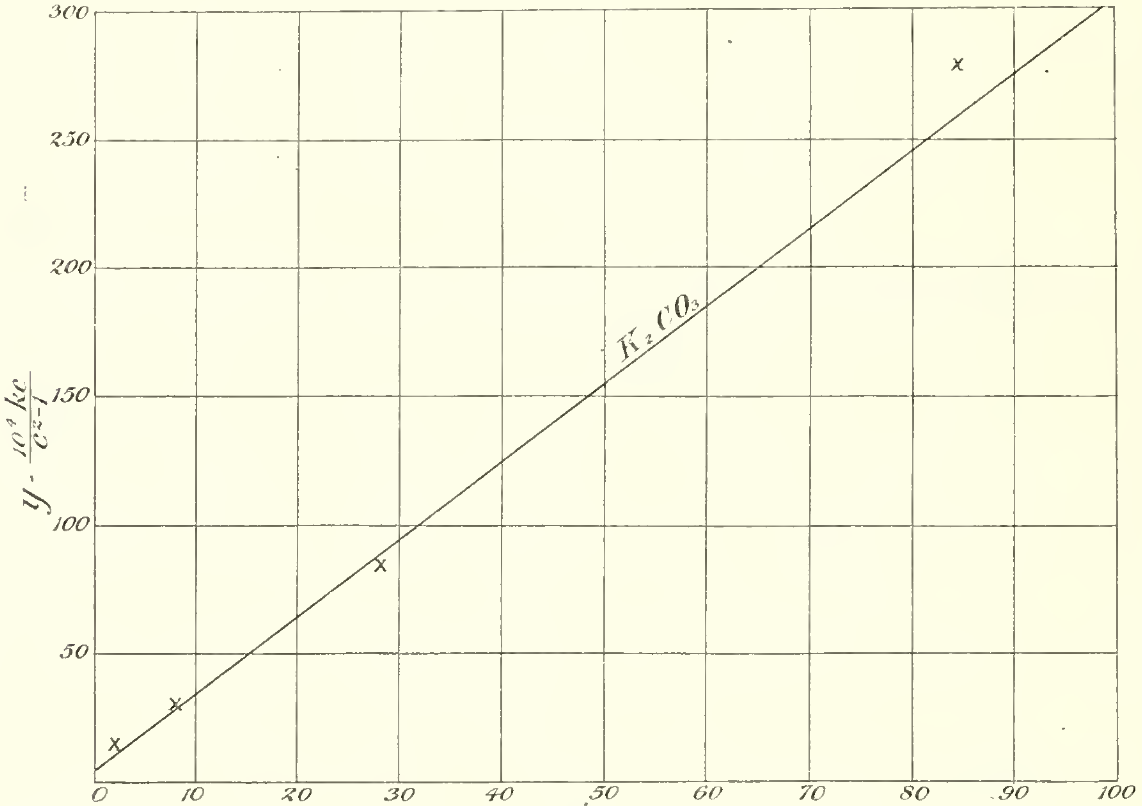

Fig 8

Let there be S molecules of one salt and S′ of the other present per cubic centimetre in the flame. Let the first salt produce n positive ions per cubic centimetre, and the second n'. We have

$$S-n = \alpha n(n+n'+m),$$

$$S'-n' = \alpha' n'(n+n'+m),$$

$$F = \beta m(n+n'+m),$$

$$Ac = n+n'+m.$$

Here F, m and β relate to the flame as before. These equations give

$$A\frac{c^2-1}{c}=\frac{S}{1+\alpha Ac}+\frac{S'}{1+\alpha' Ac}$$

where c is taken equal to unity when

$$S=S'=0.$$

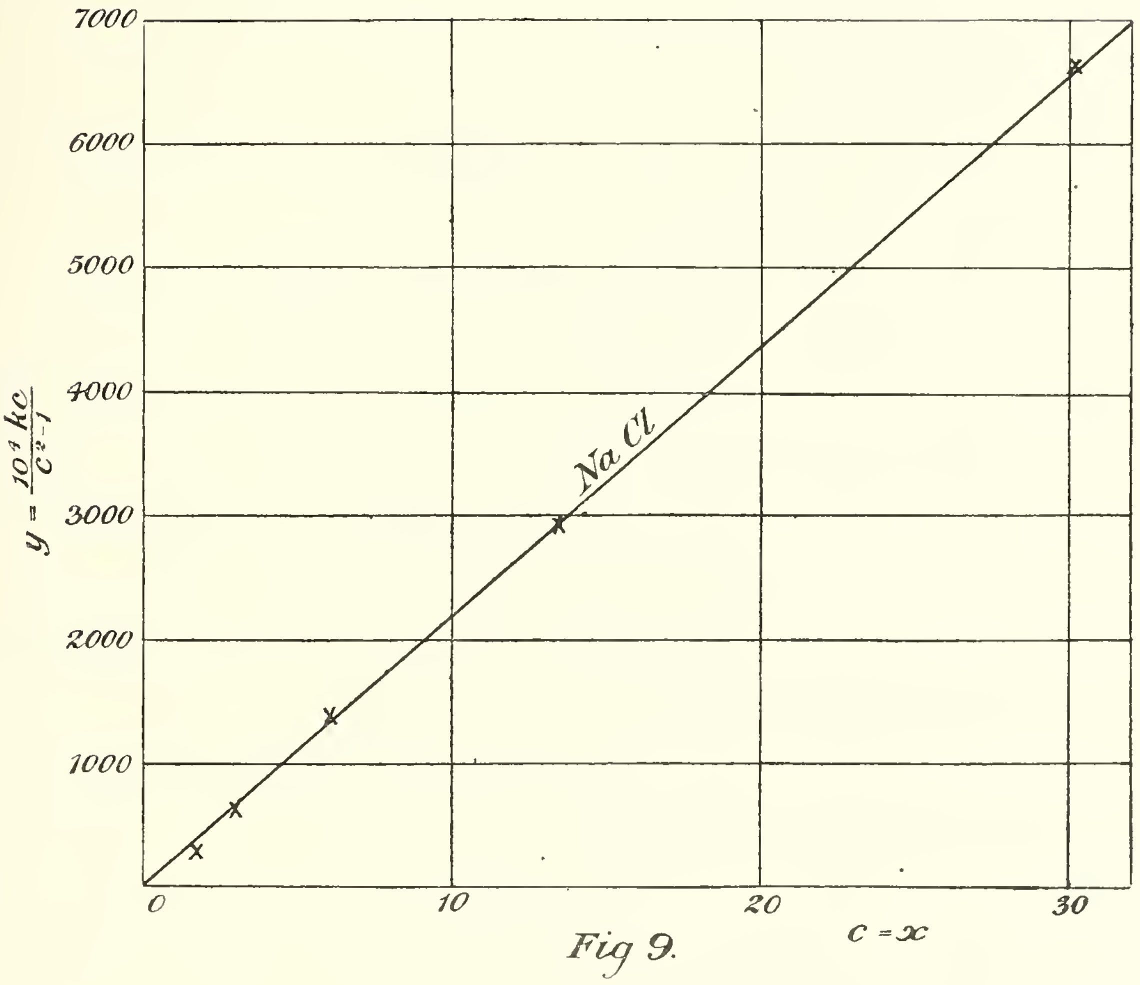

Fig 9.

Let $10^4k = GS$, $10^4k' = G'S'$, $b = GA$, $b' = G'A$, $a = G\alpha A^2$, and $a' = G'\alpha' A^2$, so that

$$\frac{c^2-1}{c}=\frac{10^4k}{b+ac}+\frac{10^4k'}{b'+a'c}.$$

To test this equation the conductivity, due to a solution of 9·06 gr. Na_2CO_3 and 0·164 gr. K_2CO_3 in a litre, was compared with that due to a solution of 18·12 gr. of Na_2CO_3 in a litre. The first solution gave a conductivity equal to 1·06 times that of the second. For the second solution $c = 30·3$, so that c for the mixture was 32·2. The above equation gives $c = 31·55$. The sum of the conductivities due to the Na_2CO_3 and K_2CO_3 when not mixed is 44·6.

PART VI.—SUMMARY OF RESULTS AND CONCLUSION.

The chief results obtained are as follows:—

(1.) The luminous vapours of salts in a Bunsen flame are not deflected appreciably by an electric field.

(2.) The positive ions present in the luminous vapour can be made to move out of it by an electric field.

(3.) The positive ions are not luminous, but can form luminous vapour after recombination.

(4.) The velocity of the positive salt ions in flames is about 1 cm. per second for 1 volt per centimetre and is the same for all salts.

(5.) The conductivity and luminosity of sodium chloride both vary nearly as the square root of the concentration of the salt vapour in the flame.

(6.) The conductivities and luminosities of chemically equivalent amounts of sodium chloride and sodium carbonate are equal.

(7.) A considerable excess of hydrochloric acid does not change the luminosity due to sodium chloride and slightly increases the conductivity of the flame.

(8.) A large excess of hydrochloric acid obtained by the introduction of chloroform vapour diminishes the luminosity due to NaCl about 50 per cent., and diminishes the conductivity about six times. The percentage changes in the luminosity and conductivity are independent of the concentration of the NaCl vapour.

(9.) The $CHCl_3$ increases the current due to large potential differences, but diminishes the conductivity as measured by the ratio of the current to the uniform potential gradient in the flame.

(10.) When the drop of potential at the negative electrode is got rid of by putting K_2CO_3 on it, the $CHCl_3$ diminishes the current to about the same extent as the conductivity.

(11.) The presence of a large amount of K_2CO_3 does not change the luminosity due to Na_2CO_3, although the K_2CO_3 greatly increases the total conductivity.

(12.) The variation of the conductivity (c) with the concentration (k) for alkali salts can be represented by the equation $10^4k = \frac{c^2-1}{c}(b+ac)$, using proper values of the constants a and b for each salt.

(13.) The equation $10^4k = \frac{c^2-1}{c}(b+ac)$ can be deduced from the ionic theory and the fraction of the salt molecules which are ionised is equal to $b/(b+ac)$.

(14.) Alkaline chlorides and carbonates impart equal conductivities to the flame for chemically equivalent concentrations.

(15.) The percentage of the salt which is ionised when the concentration is very small has the following values :—

Cæsium salts	91
Rubidium salts	69
Potassium salts	58
Sodium salts	1·6

(16.) The constant, b, is proportional to the molecular weight of the salt. According to the theory this shows that all salts give negative ions having the same velocity due to an electric field.

(17.) The conductivity due to solutions containing a mixture of salts agrees with that to be expected on the ionic theory.

It is probable that the luminous salt vapours are not appreciably moved by an electric field because very few of the salt molecules which become luminous, while the salt passes through the flame, also get ionised.

If f denotes the fraction of the salt molecules which are ionised in the flame at any instant, then $fk\mathrm{X}$ will be the average velocity of a salt molecule over a long time due to an electric field. Now f for sodium is very much smaller than for cæsium, yet both give positive ions, having about the same velocity. We conclude, therefore, that the ionic velocities observed are not of the values of $fk\mathrm{X}$, but the maximum possible velocities $k\mathrm{X}$. It follows that when a salt molecule ionises, the ions sometimes last long enough for their velocity to be measured before they recombine. The method used to measure the ionic velocities indicates the maximum velocities, not the average velocity for a large number of ions.

According to the most recent theories of ionic velocity, the velocity depends chiefly on the nature of the gas in which the ions move, and not much on the mass of the ions. We should, therefore, expect k to be about the same for ions of different salts all moving in the same flame.

The fact, first discovered by Gouy and here confirmed, that the luminosity due to sodium salts varies nearly as the square root of the concentration indicates that the luminous molecules are produced by a binary reaction from the sodium salt.

If the luminosity is due to atoms of sodium, a possible reaction is $Na_2O+CO = 2Na+CO_2$.

CO and CO_2 are both present in large quantities in the flame, so that their concentrations may be regarded as constants, and therefore the concentration of the Na will vary as the square root of the concentration of the Na_2O. Probably nearly all the salt is converted into Na_2O in the flame so that the concentration of the salt is proportional to the concentration of the Na_2O, when the concentration is not very small.

It seems probable that adding HCl to the flame does not prevent the conversion of NaCl into Na_2O by the flame gases. Otherwise, HCl should diminish the luminosity by an amount depending on the ratio of the concentration of the sodium to the concentration of the HCl. It appears that the reaction $Na_2O + 2HCl = 2NaCl + H_2O$ does not proceed appreciably at the temperature of the flame. The small effect which the HCl has on the luminosity is probably due to the change in the temperature of the flame together, possibly, with other causes.

The effect of the HCl on the conductivity was also independent of the ratio of the concentrations of the sodium and HCl. It follows, as for the luminosity, that the effect must be due to the change in the nature of the flame produced by the HCl and not to chemical action of the HCl on the sodium salts. Possibly the HCl condenses on the negative ions, so diminishing their velocity.

The effect of the HCl on the fall of potential at the negative electrode may be due to its causing the electrode to emit negative electrons.

In the earlier experiments of SMITHELLS, DAWSON, and the writer, it was found that at large concentrations oxysalts gave greater currents than haloid salts. The present experiments show that the conductivity is the same for haloid and oxysalts at all concentrations. It follows that the oxysalts diminish the fall of potential at the negative electrode when present in large quantities, while the haloid salts do not do so to the same extent. The amount of salt which entered the flame in the present experiments was rather greater than in the earlier experiments, for solutions of equal concentration.

The present experiments on the variation of the conductivity with the concentration can be explained in a satisfactory way on the ionic theory, and they confirm the view that all salts give negative ions, having equal velocities in the flame.

The fact that K_2CO_3 does not diminish the luminosity due to Na_2CO_3 seems to show conclusively that the luminosity is not due to positive ions. The K_2CO_3 increased the number of negative ions about nine times, and, therefore, must have diminished the number of positive sodium ions in the same ratio. That the negative ions from K_2CO_3 do combine with the positive ions from Na_2CO_3 is shown by the fact that the conductivity of a mixture of sodium and potassium carbonates is less than the sum of their separate conductivities as it should be according to the ionic theory.

In conclusion, I wish to say that my thanks are due to the trustees of the Rice Institute for the facilities for experimental work which they have provided.

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BY

SIR W. DE W. ABNEY, K.C.B., D.C.L., D.Sc., F.R.S.,

AND

PROF. W. WATSON, D.Sc., F.R.S.

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III. *The Threshold of Vision for Different Coloured Lights.*

By Sir W. de W. Abney, *K.C.B., D.C.L., D.Sc., F.R.S., and*
Prof. W. Watson, *D.Sc., F.R.S.*

Received June 4,—Read June 17, 1915.

1. The question as to the sensitiveness of the different regions of the retina to light of various wave-lengths is one which has received a considerable amount of attention. The results obtained by previous observers, while being in agreement in certain particulars, yet differ materially in others. For instance, the question as to whether dark adaptation takes place at the fovea and the controversy as to whether there is a failure of the secondary image at the fovea may be cited. In the course of some other experiments we were led to investigate certain differences which existed between our own eyes. The results obtained seem to throw a very considerable amount of light on the differences obtained by previous workers as well as to give interesting information as to the action of the retina.

Our results support the idea that we have to do with two distinct processes when considering the variation in the sensations produced by light, a view which was first put forward by Parinaud and has been elaborated by von Kries. The latter further identifies the rods and cones respectively as the two receptive elements of the retina. He supposes that the cones are responsible for all sensations of colour and are chiefly operative at medium and high illuminations. The rods he supposes are chiefly operative at low illuminations and only to come into action when the illumination is so low that all perception of colour is wanting, so that whatever the wave-length of the light stimulus the sensation produced is one corresponding to white or grey. Although our experiments do not provide any evidence as to the identification of the rods and cones with these two forms of vision, yet it saves so much circumlocution to speak of the sensation due to the cones or rods as the case may be that we shall use the terminology of von Kries. Thus when we speak of the sensation due to the rods we must be understood to mean the sensation due to that mechanism, whatever it is, which is alone operative at low illuminations in the central part of the retina, and similarly for the sensation due to the cones.

[Published December 6, 1915.

2. *Threshold of Light. Extinction Curves.*

A series of experiments have been made to determine the minimum intensity of light of the various colours which can be perceived when received on the fovea and at different distances from its centre up to 10 degrees. The chief difficulty in obtaining these measurements was to ensure correct fixation and to avoid retinal fatigue. Experiment showed that both these difficulties were very much reduced if the stimulus light in place of being continuously in action was only applied for a short time, say about a second, with a comparatively long interval between flashes.

With a Nernst light the arrangement employed is a slight modification of the arc colour-patch apparatus. It is shown diagrammatically in fig. 1. The source of light, a Nernst glower, A, is enclosed in a blackened metal box which has a small rectangular opening, the width of this opening being such that the glower is not screened from the collimator lens, C, and the height of the opening being such as to give a convenient width of spectrum. No collimator slit was employed, the glower itself acting as the slit and being placed at the principal focus of the lens, C. The dispersion train consists of two 60° prisms, D. A lens, E, forms a pure spectrum in the plane, FG, of a slide which carries a slit by means of which any required colour can be isolated. The position of this slit is read by means of a transparent scale attached to the slide,

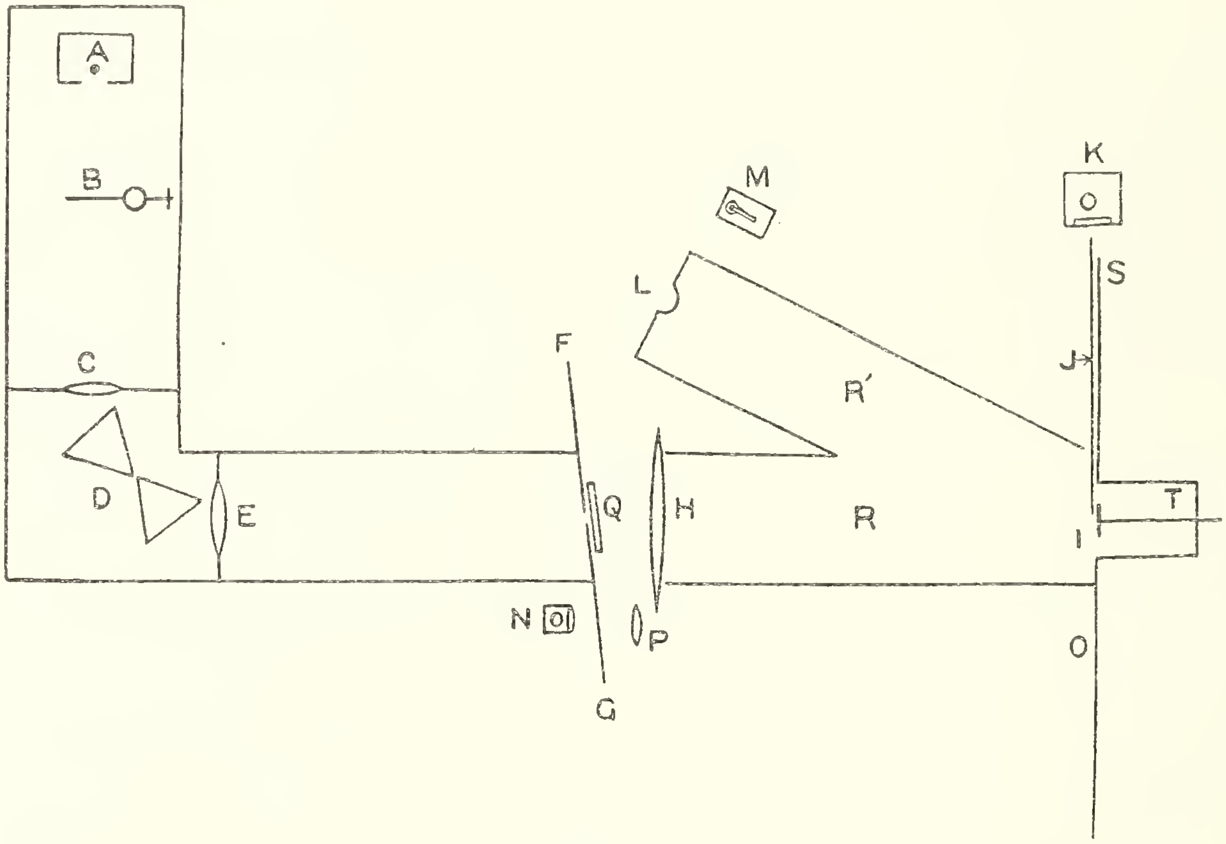

Fig. 1.

an image of this scale being projected by means of a lamp, M, and lens, P, on to a card fixed at O to a screen, OS, covered with black velvet. Attached to the slide, FG, is an annulus, Q, which has been described by one of us in a previous paper ('Phil. Trans.,' A, 190, 156, 1897). This annulus consists of a uniformly increasing wedge of gelatine impregnated with finely divided lamp black. The annulus can be rotated by means of a milled head attached to a pinion which engages with a circular rack attached to the glass carrying the annulus. A graduated circle is also attached so that the part of the annulus opposite the slit can be identified. The light after passing through the annulus is received by a large lens, H, which forms an image of the front face of the prism train in the plane of the screen, OS. This image is received on a metal disc, I, which is covered with magnesium oxide.* The velvet-lined recess, T, is of such a depth that the light which misses the disc, I, and strikes the back of the recess and might be reflected from it, cannot reach the eye of the observer who is at L. Tunnels, R and R′, lined with black velvet are used to screen off any stray light. Further, the Nernst light, prisms, &c., are all enclosed in boxes which are painted dead black inside. The instrument is placed in a room which can be rendered entirely dark. Small 3-candle power electric lamps, which are themselves screened and only switched on when required, are used to make the necessary readings of the annulus. These readings are made by an assistant who also keeps the current passing through the Nernst lamp constant.

Between the Nernst glower and the collimator lens is placed a pivoted screen, B, which normally cuts off the light from the collimator lens. By pressing a key, M, placed near the observer's hand, the screen, B, is raised by an electro-magnet. Thus the light only reaches the disc, I, when the observer presses the key, while by turning the milled head attached to the annulus he can alter the intensity of the light which falls on the disc, I. To give a fixation spot a rod of glass, J, is drawn down at the end to a diameter of about a millimetre and ground off at about 45 degrees. A small electric lamp, K, enclosed in a box with a small window covered with red glass, is placed opposite the end of this rod. The light from the lamp passes down the glass rod and owing to internal reflections does not escape from the sides till it reaches the ground end. At this end the light is scattered and thus gives a small source of red light. (By means of a resistance in the circuit of the lamp the intensity of this fixation light can be adjusted.) When fixation is desired for the central part of the retina, the circuits are so arranged that on depressing the key, M, the lamp, K, is extinguished. Thus the depression of the key by the observer causes the fixation light to disappear, and at the same instant causes the coloured light to illuminate the disc, I. When working away from the fovea the fixation light is disconnected from the key, M, so that the fixation spot does not vanish when the stimulus light is turned on. The reason for using a deep red fixation light is that such a light has little or no stimulus value for the rods.

---

* Obtained by holding the disc over a piece of burning magnesium wire.

The amount by which the light coming through the slit in the spectrum is reduced owing to its passage through the annulus depends for any given position of the annulus not only on the colour of the light but also on the distance of the receiving surface, I, from the annulus. The reason is that in the first place the coefficient of absorption of the annulus is a function of the wave-length. Secondly, there is a certain small amount of light scattered by the annulus, and the amount of this scattered light which falls on the disc depends on the distance. Hence it was necessary to measure the absorption of the annulus throughout the spectrum in exactly the same relative position as that in which it is used. This calibration involved a very considerable amount of work but need not be described.

It enabled us to calculate for any wave-length and for any annulus reading what fraction of the light passing through the slit fell on the disc. The intensity of the light falling on the disc, when the slit was placed at the sodium line, was determined by comparison with a standard Hefner lamp. This lamp is very suitable for the purpose, as the colour of its light does not differ greatly from that of the D line.

The procedure adopted was for the observer, who had been in complete darkness for more than half-an-hour, to look steadily with both eyes at the fixation spot and then to press the key, M, for about a second, thus allowing the light to fall on the disc, I, for this time. If the light was visible, he then turned the annulus so as to reduce the light, and again pressed the key. This process was continued till the light was just imperceptible when the key was pressed. The circle attached to the annulus having been read, the annulus was turned so as to make the light brighter, when the setting was repeated. In general, three settings were taken at each selected wave-length.

When observing away from the fovea the fixation spot was always placed vertically above the disc on which the stimulus light was received. Unless otherwise mentioned, the disc, on which the light was received, had a diameter of 6·3 mm., and was at a distance of 72 cm. from the observer's eye, so that the angle subtended at the eye was 34 minutes.

With the fixation spot at 1·5 mm. or more away from the centre of the disc, all the observers found it quite easy to obtain consistent results. With foveal fixation, some observers required a little practice before they were able to overcome the tendency for the eye to wander. The reason for this tendency is that for most people the sensitiveness of the retina increases (except in the red), that is the threshold value decreases, rapidly as we go out from the fovea, and hence, when striving to see the last glimmer of light they instinctively shift the axis of the eye so as to bring the image on the more sensitive area surrounding the fovea. The curves shown in fig. 2 illustrate the successive readings of the annulus obtained by one untrained observer with central fixation.* At the first attempt the numbers obtained correspond

---

* The numbers plotted in this figure are the annulus readings. The greater the annulus reading the greater the reduction in the light.

to those obtained with the fixation spot at 2·5 degrees from the fovea. At the second attempt the fixation was better but still not central. At the third attempt, the start in each case being made at the red end of the spectrum, the fixation was central down to SSN 40, after which the eye wandered slightly. During the fourth, fifth, and sixth sets of readings, the fixation was kept central throughout, and all the points obtained are in good agreement.

On the supposition that we start with a spectrum of such an intensity that the illumination on the disc when the slit is at the D line is one lux (metre-candle), we have calculated from the annulus readings by how much the light has to be reduced to reach the threshold for the different parts of the spectrum. This reduction, in conformity with the nomenclature used by one of us in previous papers, we shall call the *extinction*. The actual numbers obtained for the extinction, except of course at the D line, will depend on the distribution of light in the spectrum employed, that is on the source of light and on the dispersion curve of the prisms. In order to obtain numbers which do not involve these quantities we have determined the distribution of energy in the spectrum we have used, so that we can calculate what is the energy of the radiation falling on unit area of the disc, I, at the threshold. Since our measures of the energy are relative they give the comparative distribution of energy throughout the spectrum, but do not give the absolute values, as we have to fix an arbitrary unit. Since it is convenient to tabulate and plot the figures in the logarithms of the energy, it is advisable to avoid the use of negative characteristics,

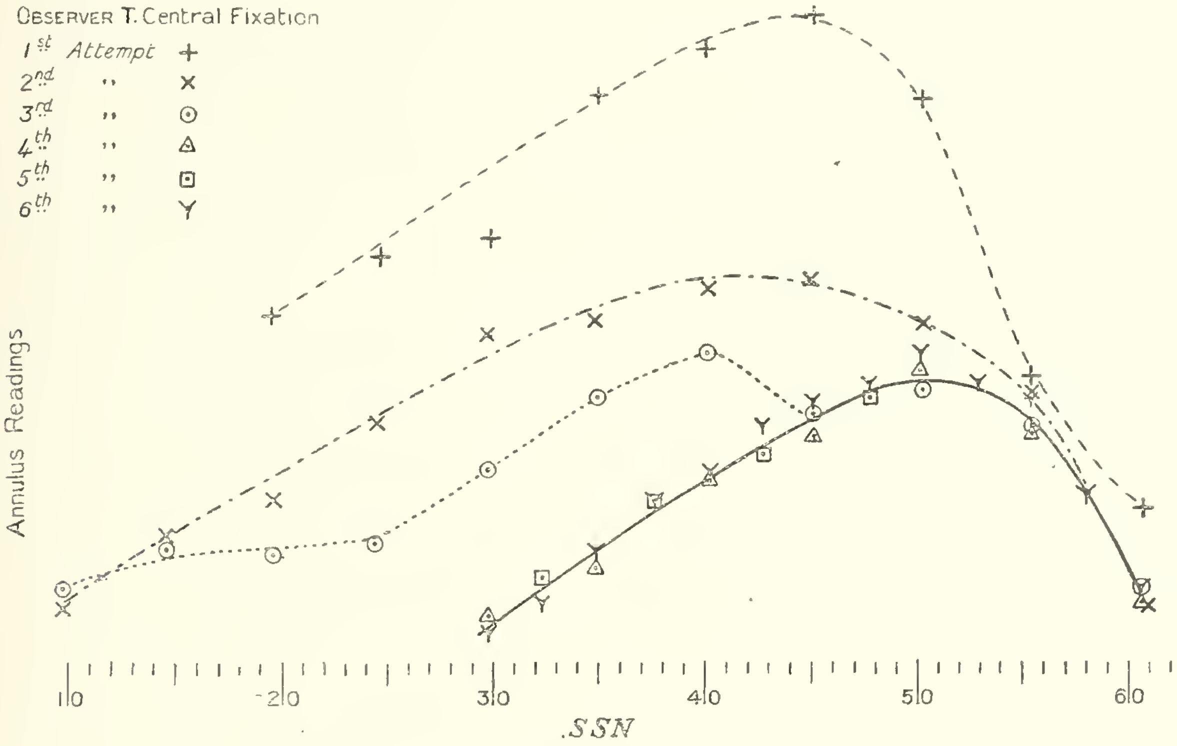

Fig. 2.

our unit is such that when the intensity of illumination by the D light on the disc, I, is one lux the energy per square centimetre is equal to 100,000 such units.

A measurement of the light diffused from the magnesium oxide surface showed that when the illumination of this surface was one lux the radiation it sends out normally per square centimetre is equal to 0·000026 candles, so that if the cosine law be assumed to hold the coefficient of reflection is 0·83.

In order to obtain the energy distribution in the spectrum, a linear thermopile was attached to the slide, FG, fig. 1, and the deflections of a sensitive galvanometer were read as the pile moved through the spectrum. In order to reduce the effect of stray heat a pair of slits were placed one in front of the other before the pile and a water cell was interposed between the Nernst glower and the collimator lens. As a test to see whether stray radiation had been eliminated, the water cell was replaced by one containing a solution of iodine in carbon bisulphide. This cell, while entirely cutting off the visible spectrum, allowed most of the infra red to pass. While there was a large deflection when the pile was placed beyond the red, there was no observable deflection while the pile moved throughout the region ordinarily occupied by the visible spectrum. Since a similar spectrum apparatus to that shown in fig. 1, except that the crater of an electric arc is the source of light, has been used for some of the experiments described in this paper, and further that it is the one used throughout the series of researches conducted by one of us for many years, we have determined the energy distribution of this source. In Table I. and fig. 3 we give the results

TABLE I.—Energy Distribution in Spectrum. Sources of Light: the Nernst Glower, and Positive Crater of Arc.

SSN.	λ ($\mu\mu$).	Energy.		SSN.	λ ($\mu\mu$).	Energy.	
		Nernst.	Arc.			Nernst.	Arc.
64	721·7	396	182	35	504·3	27·0	42·3
62	695·7	325	166	34	500·2	25·2	40·0
60	672·8	261	151	32	492·4	21·2	35·2
58	652·1	205	137	30	484·8	17·9	30·7
56	633·0	165	126	28	477·6	15·3	26·9
55	624·2	151	121	26	470·7	12·9	23·8
54	615·2	137	116	25	467·0	12·0	22·3
52	599·6	114	106	24	463·9	11·2	20·8
50	585·0	96	97	22	457·8	9·7	18·2
48	572·0	80	89	20	451·7	8·4	16·0
46	559·6	68	81	18	445·9	7·2	13·8
45	553·8	62·5	77	16	440·4	6·1	11·9
44	548·1	57	73	15	438·1	5·7	11·1
42	537·3	46·5	65·5	14	434·9	5·2	10·4
40	527·0	39·6	58	12	429·6	4·2	9·0
38	517·2	34·3	51·5	10	424·5	3·3	8·2
36	508·5	29·6	45·5				

obtained with the two instruments. In Table I. will also be found the wave-lengths corresponding to the dispersion scale, the readings of which are indicated by the letters SSN, and which are used throughout this paper to indicate the different colours.

In Table II. are given the results obtained by eight observers. Of these A. and W. are the authors, and B. is Mr. W. Bradfield, the assistant in the Colour Vision Laboratory, to whom we are very much indebted for great assistance throughout the work. Observers T., Bk., Ar. and R. were students in the advanced Physics Class, and N. is one of our colleagues. Of these observers A., W., B., T. and Bk. have normal colour vision, Ar. and N. are dichromates, Ar. being green blind (deuteranope) and N. red blind (protanope), while R. is a case of a displaced green sensation curve whose case has already been described in a previous paper ('Roy. Soc. Proc.,' A, vol. 89, 232, 1913). Observations were in each case made throughout the spectrum using central fixation, and also with the fixation spot 1·25, 2·5, 5, and 10 degrees shown above the centre of the disc on which the stimulus light was received.

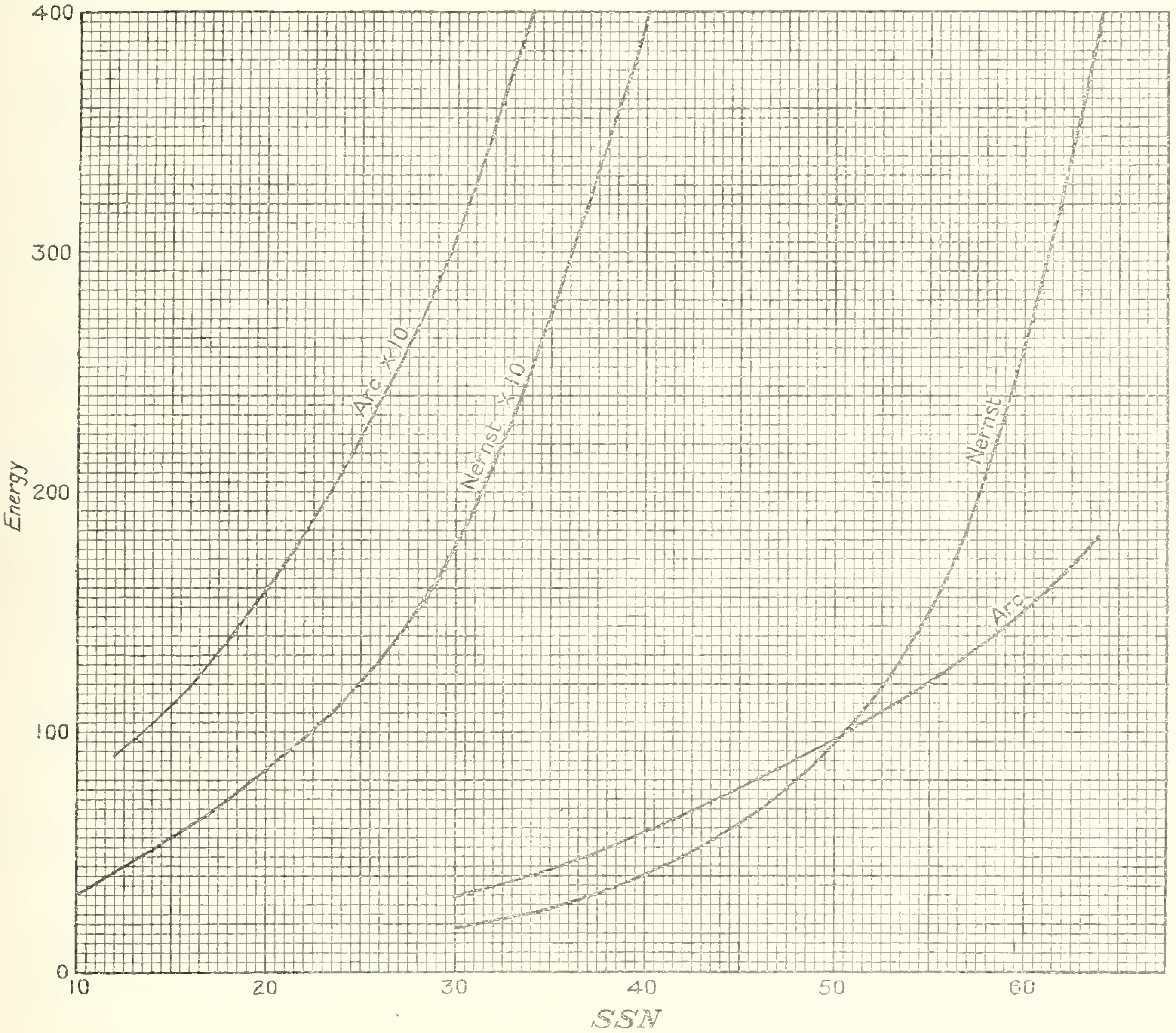

Fig. 3.

TABLE II.—Central Fixation.

Observer.	SSN . . .	10	15	20	25	30	35	40	45	50	55	60
	λ ($\mu\mu$) . . .	425	438	452	467	485	505	527	554	585	625	673
W.	log reduction .	—	—	—	—	—	$\bar{1}$·056	$\bar{2}$·498	$\bar{2}$·249	$\bar{2}$·241	$\bar{2}$·429	$\bar{1}$·152
	log energy . . .	—	—	—	—	—	3·487	3·096	3·045	3·223	3·608	4·569
Bk.	log reduction .	—	—	—	—	—	$\bar{1}$·396	$\bar{2}$·932	$\bar{2}$·519	$\bar{2}$·280	$\bar{2}$·490	$\bar{1}$·269
	log energy . . .	—	—	—	—	—	3·827	3·530	3·315	3·262	3·669	4·686
T.	log reduction .	—	—	—	—	$\bar{1}$·609	$\bar{1}$·097	$\bar{2}$·669	$\bar{2}$·279	$\bar{2}$·267	$\bar{2}$·429	$\bar{1}$·292
	log energy . . .	—	—	—	—	3·862	3·528	3·267	3·075	3·249	3·608	4·709
R.	log reduction .	—	—	—	—	—	$\bar{1}$·328	$\bar{2}$·801	$\bar{2}$·352	$\bar{2}$·180	$\bar{2}$·478	$\bar{1}$·210
	log energy . . .	—	—	—	—	—	3·759	3·399	3·148	3·162	3·657	4·627
N.	log reduction .	—	—	—	—	—	—	$\bar{1}$·090	$\bar{2}$·468	2·259	$\bar{2}$·441	
	log energy . . .	—	—	—	—	—	—	3·688	3·264	3·241	3·620	
A.	log reduction .	$\bar{2}$·849	$\bar{2}$·399	$\bar{3}$·947	$\bar{3}$·529	$\bar{3}$·185	$\bar{4}$·919	$\bar{4}$·691	$\bar{4}$·727	$\bar{3}$·135	$\bar{3}$·813	$\bar{1}$·094
	log energy . . .	2·367	2·155	1·871	1·608	1·438	1·350	1·289	1·523	2·117	2·992	4·511
B.	log reduction .	$\bar{3}$·739	$\bar{3}$·263	$\bar{4}$·752	$\bar{4}$·398	$\bar{4}$·058	5·815	5·689	$\bar{5}$·755	$\bar{4}$·290	$\bar{3}$·305	$\bar{2}$·625
	log energy . . .	1·257	1·019	0·676	0·477	0·311	0·246	0·287	0·551	1·272	2·484	4·042
Ar.	log reduction .	$\bar{1}$·230	$\bar{2}$·870	$\bar{2}$·499	$\bar{2}$·111	$\bar{3}$·847	$\bar{3}$·627	$\bar{3}$·509	$\bar{3}$·675	$\bar{2}$·068	$\bar{2}$·574	$\bar{1}$·303
	log energy . . .	2·748	2·626	2·423	2·190	2·100	2·058	2·107	2·471	3·050	3·753	4·720

10 degrees from Fovea.

Observer.	SSN . . .	10	15	20	25	30	35	40	45	50	55	60
W.	log reduction .	$\bar{2}$·348	$\bar{3}$·840	3·380	$\bar{3}$·038	$\bar{4}$·691	$\bar{4}$·458	$\bar{4}$·320	$\bar{4}$·498	$\bar{3}$·160	$\bar{2}$·271	$\bar{1}$·444
	log energy . . .	1·866	1·591	1·304	1·117	0·944	0·889	0·918	1·294	2·142	3·450	4·861
Bk.	log reduction .	$\bar{2}$·438	$\bar{3}$·959	$\bar{3}$·468	$\bar{3}$·065	$\bar{4}$·706	$\bar{4}$·486	$\bar{4}$·359	$\bar{4}$·485	$\bar{4}$·973	$\bar{2}$·042	$\bar{1}$·187
	log energy . . .	1·956	1·715	1·392	1·144	0·959	0·887	0·957	1·281	1·955	3·221	4·604
T.	log reduction .	$\bar{2}$·956	$\bar{2}$·551	$\bar{2}$·141	$\bar{3}$·719	$\bar{3}$·283	$\bar{3}$·014	$\bar{4}$·916	$\bar{3}$·163	$\bar{3}$·807	$\bar{2}$·634	$\bar{1}$·444
	log energy . . .	2·474	2·307	2·065	1·798	1·536	1·445	1·514	1·959	2·789	3·813	4·861
R.	log reduction .	$\bar{2}$·895	$\bar{2}$·399	$\bar{3}$·947	$\bar{3}$·539	$\bar{3}$·199	$\bar{4}$·905	$\bar{4}$·850	$\bar{3}$·113	$\bar{3}$·595	$\bar{2}$·331	$\bar{1}$·503
	log energy . . .	2·413	2·155	1·871	1·618	1·452	1·336	1·448	1·909	2·577	3·510	4·920
N.	log reduction .	$\bar{2}$·682	$\bar{2}$·142	$\bar{3}$·753	$\bar{3}$·416	$\bar{3}$·115	$\bar{4}$·878	$\bar{4}$·744	$\bar{4}$·881	$\bar{3}$·458	$\bar{2}$·550	
	log energy . . .	2·200	1·898	1·677	1·495	1·368	1·309	1·342	1·677	2·440	3·729	
A.	log reduction .	$\bar{2}$·728	$\bar{2}$·278	$\bar{3}$·755	$\bar{3}$·283	$\bar{4}$·875	$\bar{4}$·565	$\bar{4}$·399	$\bar{4}$·558	$\bar{3}$·222	$\bar{2}$·416	$\bar{1}$·444
	log energy . . .	2·246	2·034	1·679	1·362	1·128	0·996	0·997	1·354	2·204	3·595	4·861
B.	log reduction .	$\bar{2}$·240	$\bar{3}$·641	$\bar{3}$·050	$\bar{4}$·658	$\bar{4}$·339	$\bar{4}$·129	$\bar{4}$·069	$\bar{4}$·178	$\bar{4}$·662	$\bar{3}$·813	$\bar{1}$·093
	log energy . . .	1·758	1·397	0·974	0·737	0·592	0·560	0·667	0·974	1·644	2·992	4·510
Ar.	log reduction .	$\bar{2}$·485	$\bar{2}$·068	$\bar{3}$·602	$\bar{3}$·211	$\bar{4}$·875	$\bar{4}$·688	$\bar{4}$·584	$\bar{4}$·766	$\bar{3}$·458	$\bar{2}$·598	$\bar{1}$·526
	log energy . . .	2·003	1·824	1·526	1·290	1·128	1·119	1·182	1·562	2·440	3·777	4·943

TABLE II. (continued).

5 degrees from Fovea.

Observer.	SSN . . .	10	15	20	25	30	35	40	45	50	55	60
W.	log reduction .	$\bar{2}\cdot256$	$\bar{3}\cdot748$	$\bar{3}\cdot275$	$\bar{4}\cdot918$	$\bar{4}\cdot593$	$\bar{4}\cdot374$	$\bar{4}\cdot253$	$\bar{4}\cdot380$	$\bar{3}\cdot073$	$\bar{2}\cdot184$	$\bar{1}\cdot374$
	log energy . . .	1·774	1·505	1·199	0·997	0·846	0·805	0·851	1·176	2·055	3·363	4·791
Bk.	log reduction .	$\bar{2}\cdot240$	$\bar{3}\cdot760$	$\bar{3}\cdot305$	$\bar{4}\cdot891$	$\bar{4}\cdot537$	$\bar{4}\cdot239$	$\bar{4}\cdot151$	$\bar{4}\cdot331$	$\bar{4}\cdot813$	$\bar{3}\cdot909$	$\bar{1}\cdot093$
	log energy . . .	1·758	1·516	1·229	0·970	0·790	0·670	0·749	1·127	1·795	3·088	4·510
T.	log reduction .	$\bar{2}\cdot469$	$\bar{3}\cdot899$	$\bar{3}\cdot453$	$\bar{4}\cdot978$	$\bar{4}\cdot593$	$\bar{4}\cdot402$	$\bar{4}\cdot257$	$\bar{4}\cdot331$	$\bar{4}\cdot912$	$\bar{3}\cdot994$	$\bar{1}\cdot151$
	log energy . . .	1·987	1·655	1·377	1·057	0·846	0·833	0·855	1·127	1·894	3·173	4·568
R.	log reduction. .	$\bar{2}\cdot803$	$\bar{2}\cdot324$	$\bar{3}\cdot902$	$\bar{3}\cdot500$	$\bar{3}\cdot143$	$\bar{4}\cdot824$	$\bar{4}\cdot639$	$\bar{4}\cdot740$	$\bar{3}\cdot471$	$\bar{2}\cdot453$	$\bar{1}\cdot327$
	log energy . . .	2·321	2·080	1·826	1·579	1·396	1·255	1·237	1·536	2·453	3·632	4·744
N.	log reduction	$\bar{2}\cdot697$	$\bar{2}\cdot172$	$\bar{3}\cdot723$	$\bar{3}\cdot309$	$\bar{4}\cdot974$	$\bar{4}\cdot728$	$\bar{4}\cdot491$	$\bar{4}\cdot580$	$\bar{3}\cdot196$	$\bar{2}\cdot271$	
	log energy . . .	2·215	1·928	1·647	1·388	1·227	1·159	1·089	1·376	2·178	3·450	
A.	log reduction .	$\bar{2}\cdot895$	$\bar{2}\cdot369$	$\bar{3}\cdot872$	$\bar{3}\cdot428$	$\bar{3}\cdot016$	$\bar{4}\cdot742$	$\bar{4}\cdot519$	$\bar{4}\cdot561$	$\bar{3}\cdot322$	$\bar{2}\cdot393$	$\bar{1}\cdot655$
	log energy . . .	2·413	2·125	1·796	1·507	1·269	1·173	1·117	1·357	2·304	3·572	5·072
B.	log reduction .	$\bar{2}\cdot145$	$\bar{3}\cdot643$	$\bar{3}\cdot155$	$\bar{4}\cdot731$	$\bar{4}\cdot368$	$\bar{4}\cdot129$	$\bar{5}\cdot980$	$\bar{4}\cdot113$	$\bar{4}\cdot675$	$\bar{3}\cdot788$	$\bar{1}\cdot035$
	log energy . . .	1·713	1·399	1·079	0·810	0·621	0·560	0·578	0·909	1·657	2·967	4·452
Ar.	log reduction .	$\bar{2}\cdot756$	$\bar{2}\cdot340$	$\bar{3}\cdot901$	$\bar{3}\cdot502$	$\bar{3}\cdot156$	$\bar{4}\cdot920$	$\bar{4}\cdot756$	$\bar{4}\cdot933$	$\bar{3}\cdot482$	$\bar{2}\cdot671$	$\bar{1}\cdot503$
	log energy . . .	2·274	2·096	1·825	1·581	1·409	1·351	1·354	1·729	2·464	3·850	4·920

$2\frac{1}{2}$ degrees from Fovea.

Observer.	SSN . . .	10	15	20	25	30	35	40	45	50	55	60
W.	log reduction .	$\bar{2}\cdot693$	$\bar{2}\cdot172$	$\bar{3}\cdot751$	$\bar{3}\cdot341$	$\bar{3}\cdot017$	$\bar{4}\cdot728$	$\bar{4}\cdot599$	$\bar{4}\cdot715$	$\bar{3}\cdot347$	$\bar{2}\cdot272$	$\bar{1}\cdot304$
	log energy . . .	2·211	1·928	1·675	1·420	1·270	1·159	1·197	1·511	2·329	3·451	4·721
Bk.	log reduction .	$\bar{2}\cdot622$	$\bar{2}\cdot111$	$\bar{3}\cdot648$	$\bar{3}\cdot167$	$\bar{4}\cdot834$	$\bar{4}\cdot474$	$\bar{4}\cdot244$	$\bar{4}\cdot484$	$\bar{4}\cdot998$	$\bar{2}\cdot042$	$\bar{1}\cdot234$
	log energy . . .	2·140	1·867	1·572	1·246	1·087	0·905	0·842	1·280	1·980	3·221	4·651
T.	log reduction .	$\bar{2}\cdot545$	$\bar{2}\cdot036$	$\bar{3}\cdot514$	$\bar{3}\cdot094$	$\bar{4}\cdot762$	$\bar{4}\cdot470$	$\bar{4}\cdot343$	$\bar{4}\cdot485$	$\bar{3}\cdot036$	$\bar{2}\cdot163$	$\bar{1}\cdot128$
	log energy . . .	2·063	1·792	1·438	1·173	1·015	0·901	1·041	1·281	2·018	3·342	4·545
R.	log reduction .	$\bar{2}\cdot805$	$\bar{2}\cdot293$	$\bar{3}\cdot841$	$\bar{3}\cdot414$	$\bar{3}\cdot016$	$\bar{4}\cdot716$	$\bar{4}\cdot454$	$\bar{4}\cdot631$	$\bar{3}\cdot284$	$\bar{2}\cdot272$	$\bar{1}\cdot427$
	log energy . . .	2·323	2·049	1·765	1·493	1·269	1·147	1·052	1·427	2·266	3·451	4·844
N.	log reduction .	$\bar{1}\cdot139$	$\bar{2}\cdot658$	$\bar{2}\cdot126$	$\bar{3}\cdot719$	$\bar{3}\cdot381$	$\bar{3}\cdot096$	$\bar{4}\cdot942$	$\bar{3}\cdot073$	$\bar{3}\cdot533$	$\bar{2}\cdot332$	
	log energy . . .	2·657	2·414	2·050	1·798	1·634	1·527	1·540	1·869	2·515	3·511	
A.	log reduction .	$\bar{2}\cdot849$	$\bar{2}\cdot409$	$\bar{3}\cdot971$	$\bar{3}\cdot530$	$\bar{3}\cdot157$	$\bar{4}\cdot769$	$\bar{4}\cdot523$	$\bar{4}\cdot689$	$\bar{3}\cdot284$	$\bar{2}\cdot188$	
	log energy . . .	2·367	2·165	1·895	1·609	1·410	1·200	1·121	1·485	2·266	3·367	
B.	log reduction .	$\bar{2}\cdot211$	$\bar{3}\cdot641$	$\bar{3}\cdot183$	$\bar{4}\cdot731$	$\bar{4}\cdot421$	$\bar{4}\cdot129$	$\bar{5}\cdot980$	$\bar{4}\cdot013$	$\bar{4}\cdot662$	$\bar{3}\cdot607$	$\bar{1}\cdot035$
	log energy . . .	1·729	1·397	1·107	0·810	0·674	0·550	0·578	0·809	1·644	2·786	4·552
Ar.	log reduction .	$\bar{1}\cdot080$	$\bar{2}\cdot658$	$\bar{2}\cdot141$	$\bar{3}\cdot648$	$\bar{3}\cdot297$	$\bar{3}\cdot055$	$\bar{4}\cdot964$	$\bar{3}\cdot200$	$\bar{3}\cdot745$	$\bar{2}\cdot731$	$\bar{1}\cdot239$
	log energy . . .	2·598	2·414	$\bar{2}\cdot065$	1·727	1·550	1·486	1·562	1·996	2·727	3·910	4·656

TABLE II. (continued).

$1\frac{1}{4}$ degrees from Fovea.

Observer.	SSN . . .	10	15	20	25	30	35	40	45	50	55	60
W.	log reduction .	$\bar{1}\cdot336$	$\bar{2}\cdot824$	$\bar{2}\cdot350$	$\bar{3}\cdot922$	$\bar{3}\cdot537$	$\bar{2}\cdot245$	$\bar{3}\cdot087$	$\bar{3}\cdot201$	$\bar{3}\cdot707$	$\bar{2}\cdot308$	$\bar{1}\cdot164$
	log energy . . .	2·854	2·580	2·274	2·001	1·790	1·676	1·685	1·997	2·689	3·487	4·581
Bk.	log reduction .	$\bar{2}\cdot926$	$\bar{2}\cdot536$	$\bar{2}\cdot126$	$\bar{3}\cdot762$	$\bar{3}\cdot396$	$\bar{3}\cdot109$	$\bar{4}\cdot887$	$\bar{4}\cdot926$	$\bar{3}\cdot483$	$\bar{2}\cdot272$	$\bar{1}\cdot152$
	log energy . . .	2·444	2·392	2·050	1·841	1·649	1·540	1·485	1·722	2·465	3·451	4·569
T.	log reduction .	$\bar{2}\cdot971$	$\bar{2}\cdot521$	$\bar{3}\cdot992$	$\bar{3}\cdot500$	$\bar{3}\cdot016$	4·715	$\bar{4}\cdot520$	$\bar{4}\cdot664$	$\bar{3}\cdot347$	$\bar{2}\cdot272$	$\bar{1}\cdot210$
	log energy . . .	2·489	2·277	1·916	1·579	1·269	1·146	1·118	1·460	2·329	3·451	4·627
R.	log reduction .	—	$\bar{1}\cdot279$	$\bar{2}\cdot858$	$\bar{2}\cdot401$	$\bar{2}\cdot002$	$\bar{3}\cdot654$	$\bar{3}\cdot440$	$\bar{3}\cdot470$	$\bar{3}\cdot819$	$\bar{2}\cdot344$	$\bar{1}\cdot210$
	log energy . . .	—	3·035	2·782	2·480	2·255	2·085	2·038	2·266	2·801	3·523	4·627
N.	log reduction .	$\bar{1}\cdot123$	$\bar{2}\cdot703$	$\bar{2}\cdot276$	$\bar{3}\cdot864$	$\bar{3}\cdot422$	$\bar{3}\cdot055$	$\bar{4}\cdot758$	$\bar{4}\cdot791$	$\bar{3}\cdot347$	$\bar{2}\cdot212$	
	log energy . . .	2·641	2·459	2·200	1·943	1·675	1·486	1·356	1·587	2·329	3·391	
A.	log reduction .	$\bar{2}\cdot499$	$\bar{3}\cdot991$	$\bar{3}\cdot499$	$\bar{3}\cdot138$	$\bar{4}\cdot734$	$\bar{4}\cdot375$	$\bar{4}\cdot189$	$\bar{4}\cdot542$	$\bar{3}\cdot197$	$\bar{3}\cdot990$	$\bar{1}\cdot096$
	log energy . . .	2·017	1·747	1·423	1·217	0·987	0·806	0·787	1·338	2·179	3·169	4·513
B.	log reduction .	$\bar{2}\cdot439$	$\bar{3}\cdot916$	$\bar{3}\cdot408$	$\bar{4}\cdot876$	$\bar{4}\cdot481$	$\bar{4}\cdot130$	$\bar{5}\cdot980$	$\bar{4}\cdot113$	$\bar{4}\cdot687$	$\bar{3}\cdot788$	$\bar{2}\cdot986$
	log energy . . .	1·957	1·672	1·332	0·955	0·734	0·561	0·578	0·909	1·669	2·967	4·403
Ar.	log reduction .	$\bar{1}\cdot351$	$\bar{2}\cdot976$	$\bar{2}\cdot545$	$\bar{2}\cdot111$	$\bar{3}\cdot650$	$\bar{3}\cdot286$	$\bar{3}\cdot074$	$\bar{3}\cdot291$	$\bar{3}\cdot844$	$\bar{2}\cdot611$	$\bar{1}\cdot362$
	log energy . . .	2·869	2·732	2·469	2·190	1·903	1·717	1·672	2·087	2·826	3·790	4·779

In fig. 4 the logarithms of the energy at the threshold are plotted against the deviations (colour) for W., while in fig. 5 the corresponding curves for B. are given. In the case of W. the curve corresponding to the fovea is very much higher, *i.e.*, the threshold is higher that for the peripheral curves, and with the intensity of spectrum used the central curve could not be traced beyond SSN 35 on the blue side. In the case of B., however, the foveal curve is lower than any of the others, showing that for this observer the threshold is lower at the fovea than for any other part of the retina, while all the curves can be traced right down to SSN 10. For W. as we proceed outwards from the fovea the threshold values, except in the red, rapidly decrease, indicating an increasing sensitiveness, up to 5 degrees, there being a slight decrease at

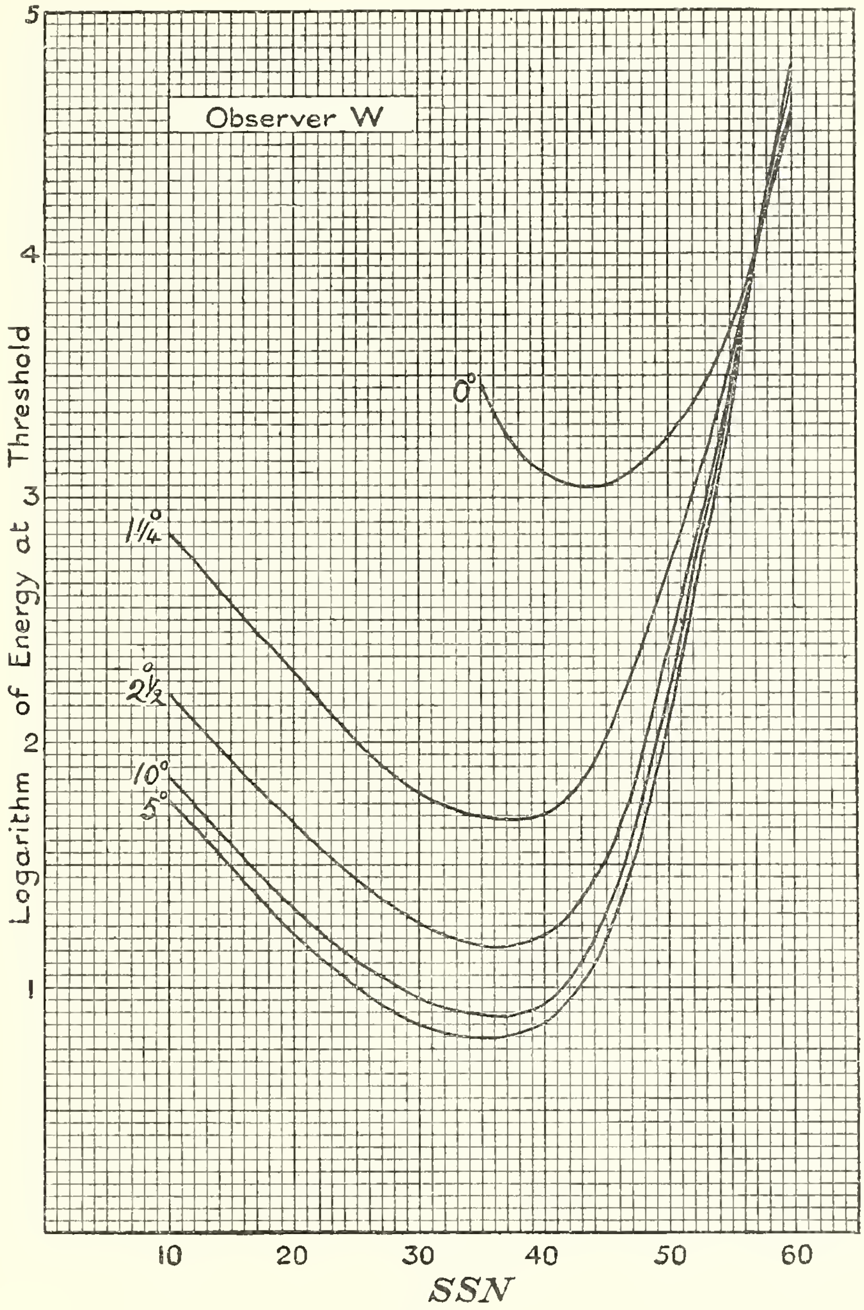

Fig. 4.

10 degrees. For B., while the threshold at the fovea is slightly lower than for the rest of the retina, the values obtained at the other distances are very nearly the same, indicating that over this region of his retina the sensitiveness remains practically constant for light of very low intensities. This peculiarity that the sensitiveness of B.'s retina for feeble lights is a maximum at the fovea has some interesting consequences. Thus he finds no difficulty in obtaining central fixation and he can obtain luminosity measurements even with very feeble intensities which are quite consistent. With W., on the contrary, central fixation with feeble lights is difficult, and when he attempts to make luminosity measurements at low intensities his results are very irregular, owing to the tendency to use the parafoveal regions of the retina, which are more sensitive than the fovea. Adopting as beforesaid for convenience VON KRIES'S

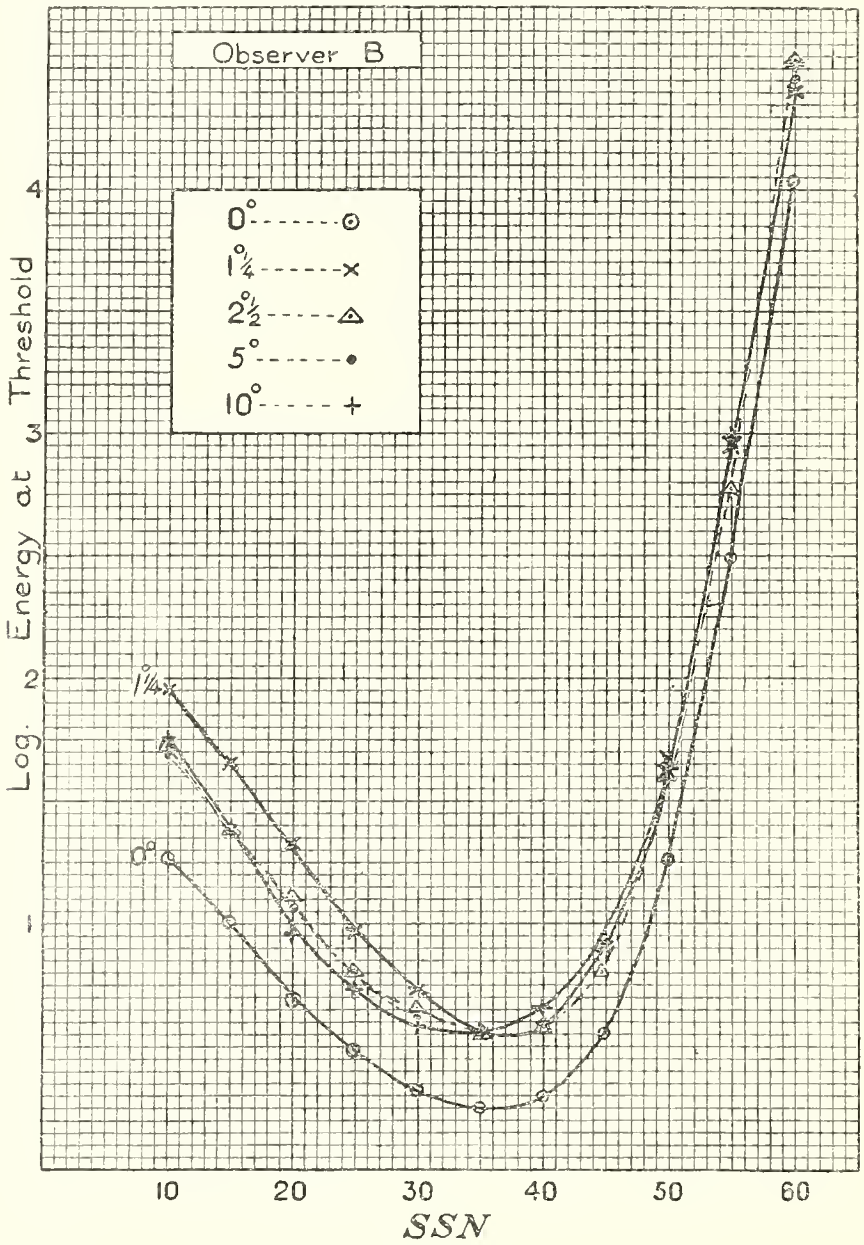

Fig. 5.

theory, the results indicate that in the case of W. the fovea is free from rods while the number of rods increase rapidly as we go from the fovea. In the case of B., however, the distribution of rods, at any rate up to at least 10 degrees, is very nearly uniform, if anything there being an excess at the fovea. It is, however, possible that the lower value for the threshold obtained at the fovea may be due to the better definition of the image formed at the fovea, so that the falling off of the sensitiveness as we go from the fovea may possibly be due to spherical aberration of the eye.

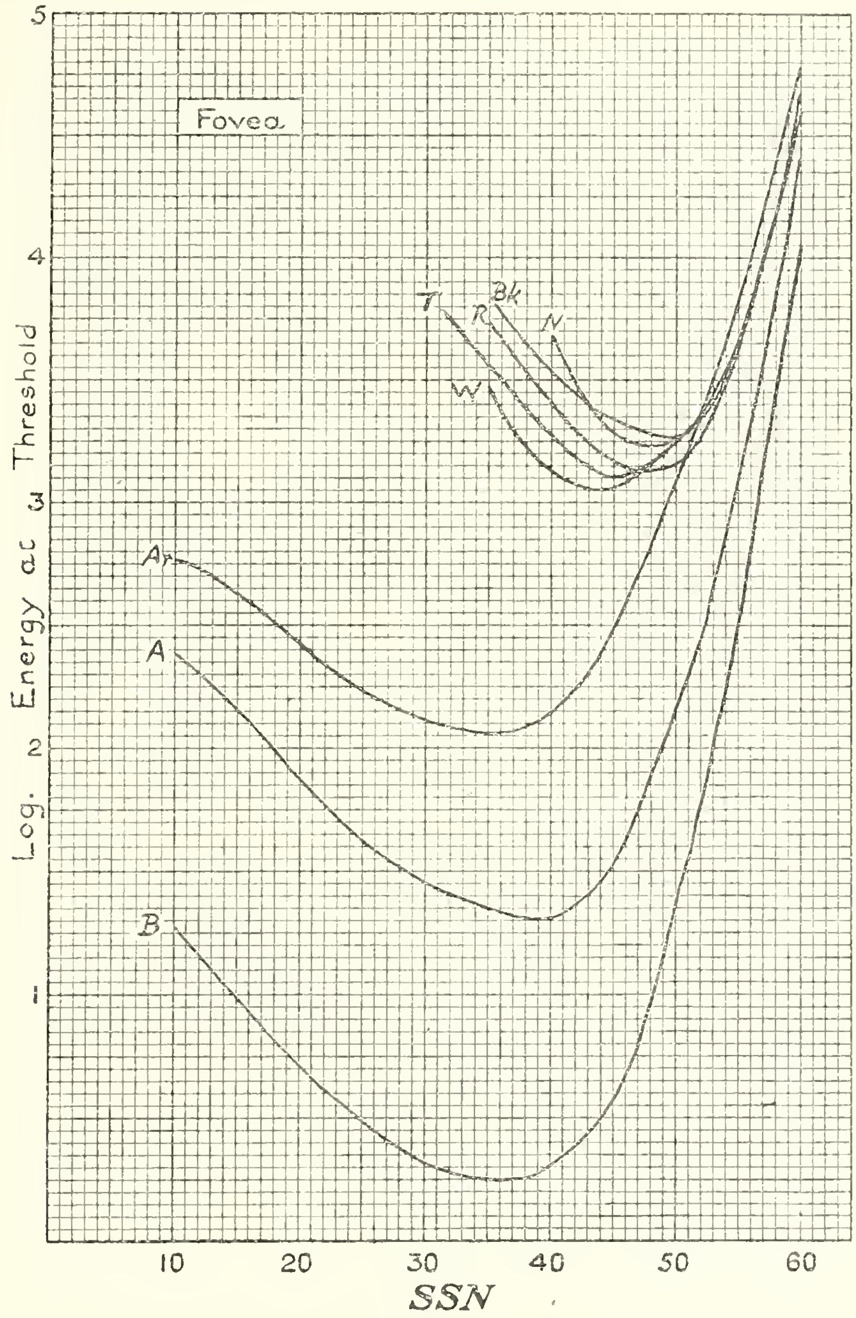

Fig. 6.

In fig. 6 the curves corresponding to the foveal measurements for all the observers are plotted together, and it will be seen that in the case of observers W., T., Bk., R. and N. the curves are in very fair agreement, and we may classify these persons as belonging to a single class, I., who have a fovea practically free from rods. Observers B., A.

and Ar. on the other hand belong to another class, II., who have a more or less plentiful supply of rods at the fovea.

Since persons belonging to class II. so far appear to be less common, and as much greater individual variation occurs in this class than in class I., we give the series of curves for the two other observers of class II. It will be noticed that in the case of A (fig. 7) the threshold values at the fovea are the highest except in the red, while the values at 1·25 degrees from the fovea are the lowest. The differences for the different parts of the region studied are not however very great, so that up to 10 degrees from the fovea the distribution of rods is fairly uniform. In the case of Ar. (fig. 8) there is a fairly uniform decrease in the threshold values as we go out from the fovea, at any rate up to 10 degrees.

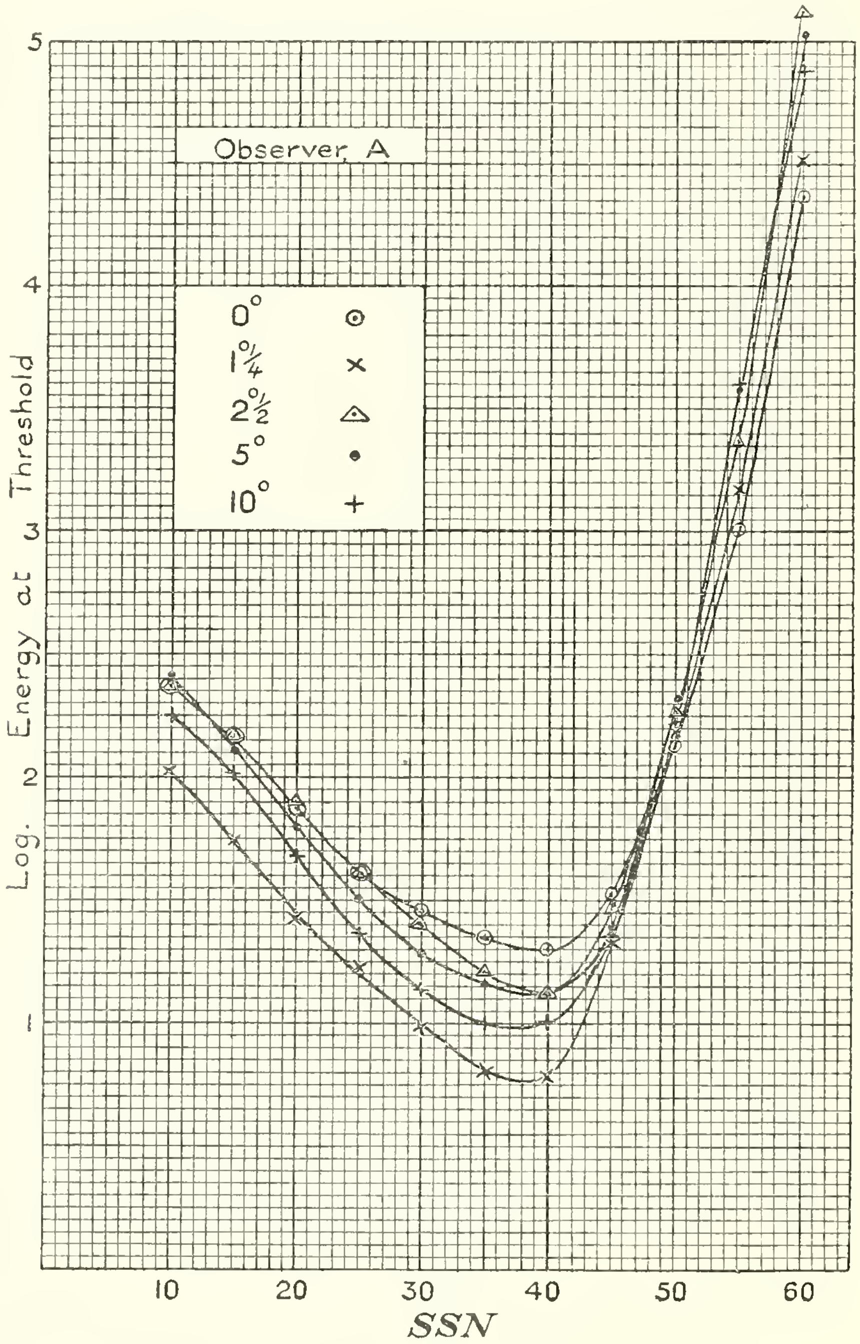

Fig. 7.

The differences obtained at the fovea between observers belonging to the two classes could be explained without supposing any distinction as to the distribution of rods if we suppose that the observers belonging to class II. did not obtain correct foveal fixation. There is, however, strong evidence that this is not the correct explanation. In the first place observers A. and B. are very expert in making this kind of observation. They can repeat their measures day after day even after many months and obtain constant values. Had there been any faulty fixation the measurements obtained would not remain constant but would be of the same nature as those illustrated in fig. 2. Further evidence that in the case of A. and B. there are rods at the fovea will be given later.

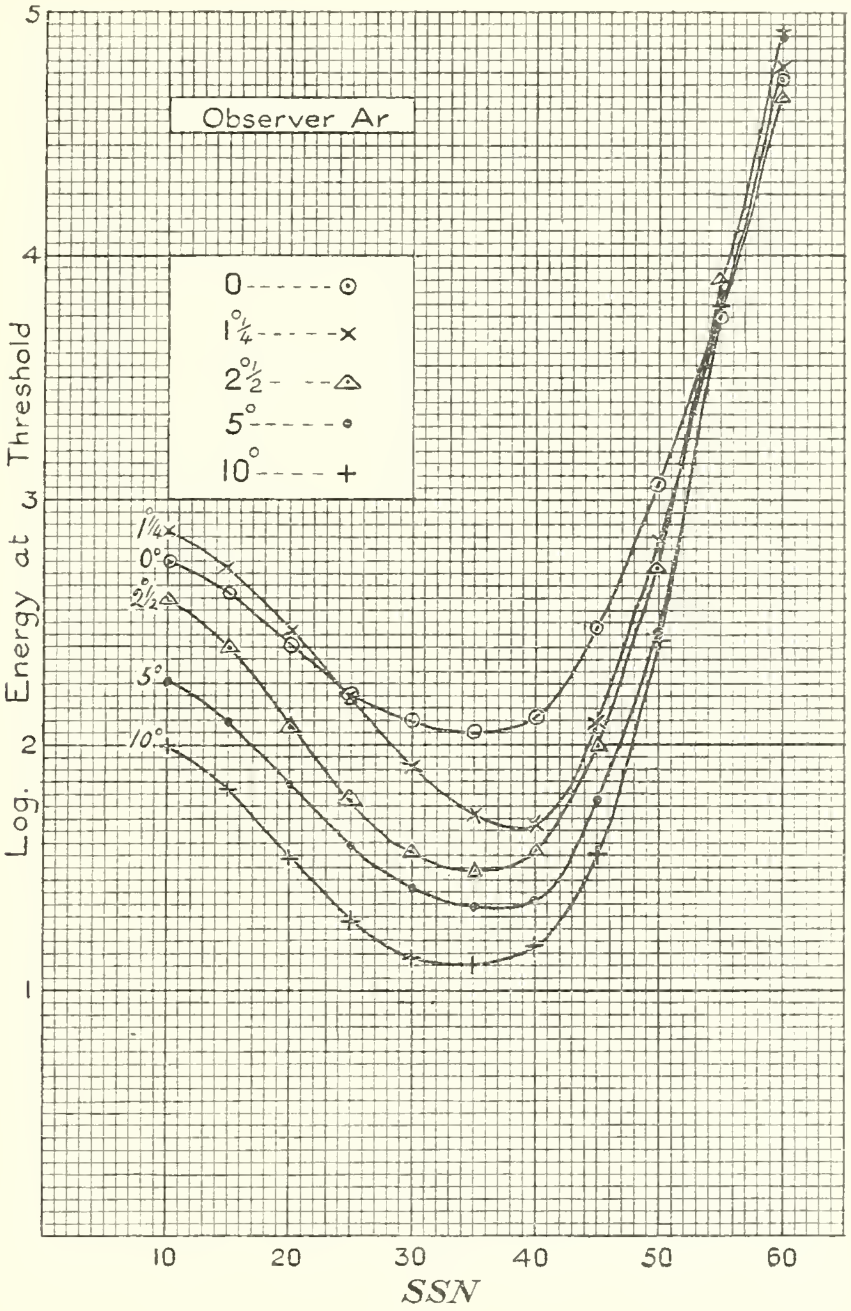

Fig. 8.

In the case of observers of class I., the light just before it is extinguished at the fovea gives the sensation of *colour*. This is particularly well marked in the green, where the faintest light observable with central fixation appears of a dull but very saturated green. In the case of observers of class II., on the other hand, as long as the stimulus light is red they can distinguish the red colour when the light is visible at all, but throughout the rest of the spectrum the light loses colour a considerable time before it is extinguished. These class II. observers have an achromatic interval throughout the whole of the spectrum except perhaps in the red.

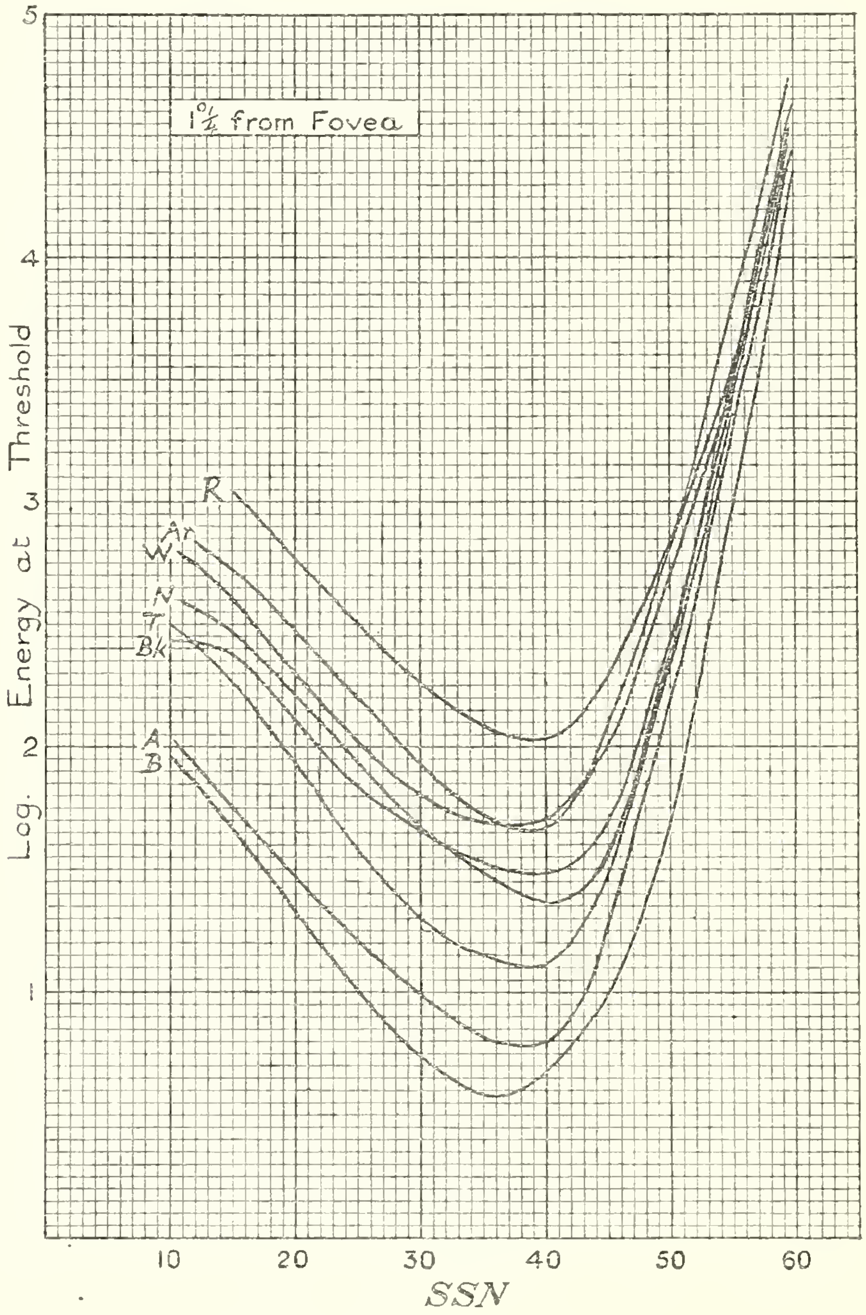

Fig. 9.

It may be remarked, that when W. attempted to determine his foveal threshold values without using the arrangements which have been described above, but employing a continuous illumination which was gradually decreased in intensity, his results were very variable, but corresponded roughly to those obtained at about 2·5 degrees from the fovea though he was under the impression that correct fixation was being secured. During the course of these observations, however, he noticed that the light sometimes appeared to vanish, and he satisfied himself that this occurred whenever he managed to bring the image on the fovea. If, when using the fixation spot and shutter for central fixation the annulus is turned till the light has vanished, say in the green, if the eye is moved a little bit on one side of the fixation spot and the shutter opened, the flash of light seen appears almost blinding.

Fig. 10.

In fig. 9 are collected together all the curves for 1·25 degrees from the fovea, and it will be noted how in the case of all observers of class I., there is a marked change from the values at the fovea, but they approximate much more nearly to those obtained by observers of class II. While the threshold values for observers A. and B. are definitely lower than any of the others, observer Ar. has at 1·25 degrees threshold values higher than those of the majority of class I.

In figs. 10, 11, and 12 are collected the threshold curves for 2·5, 5, and 10 degrees, and it will be seen that in each case there is no distinction between the two classes.

With regard to the observers having abnormal colour vision, Ar. and R. have threshold values which do not differ materially from the values obtained by persons with normal colour vision. The red blind observer N. has a markedly higher threshold value at the red end of the spectrum, in fact the spectrum employed in the measurements was not sufficiently bright for him to obtain readings beyond SSN 55 (625 $\mu\mu$). In the green, blue, and violet, his values for the threshold agree with the normal.

Fig. 11.

The threshold in the red, we are assuming, depends on the cones, and N.'s cone vision is defective since he has a shortened spectrum, hence his high threshold values at the red end.

Piper ('Zeit. f. Psychol. u. Physiol. d. Sinn.,' 32, 161, 1904; see also Helmholtz 'Physiol. Optik,' 3rd edition, vol. 2, 286) found that with the dark adapted eye, and with stimuli which approach the threshold, binocular summation occurs, so that when a feebly illuminated surface was examined with both eyes it appeared nearly twice as bright as when one eye only was used. He also found that the threshold values for the two eyes used together were about half the values for either eye used separately. It seemed of interest to examine whether this summation effect would be the same for observers of the two classes, and hence W. (class I.) and B. (class II.) made

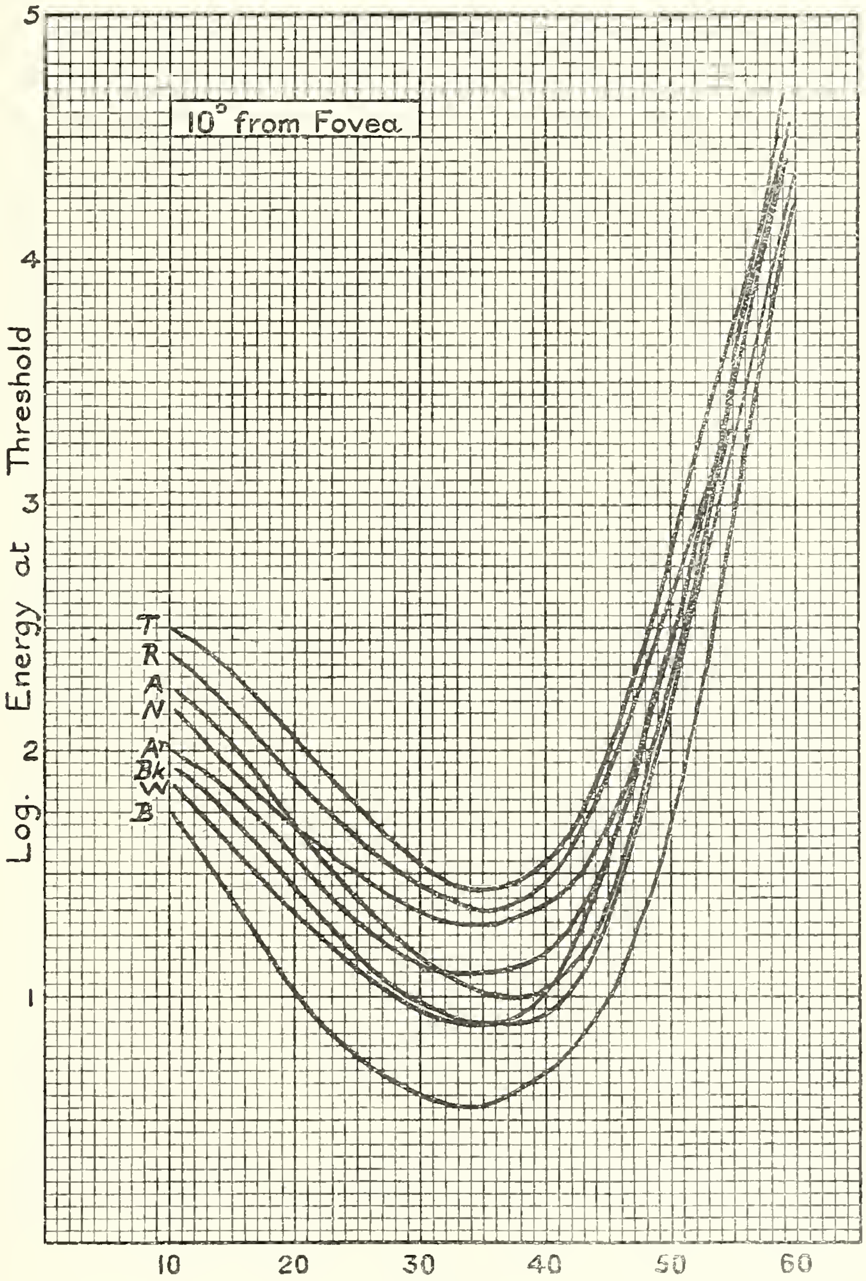

Fig. 12.

threshold observations using (1) both eyes, (2) the right eye only, and (3) the left eye only. Sets of observations were made both at the fovea and at 5 degrees from the fovea. They both found that it was much more difficult to obtain satisfactory settings when using only one eye. The difficulty appears to be due to not being able to keep the accommodation of a single eye so adjusted that the fixation light is always in focus, unless so bright a fixation light is used as to interfere with the extinction settings. The actual annulus readings obtained are plotted in figs. 13, 14, and 15. It will be seen that for W. at 5 degrees from the fovea the

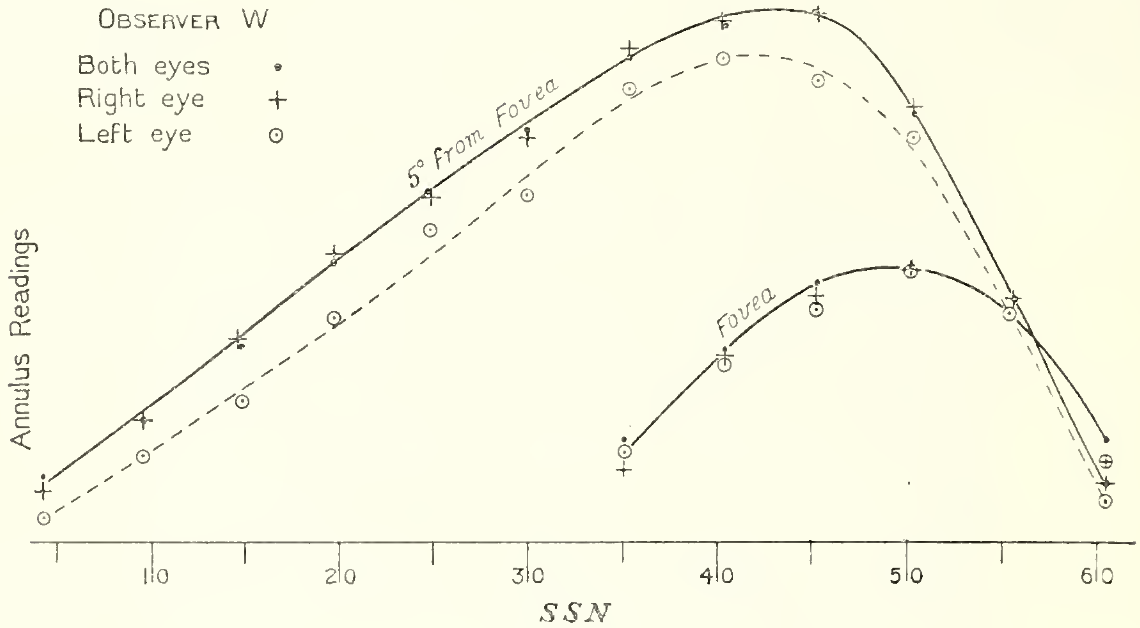

Fig. 13.

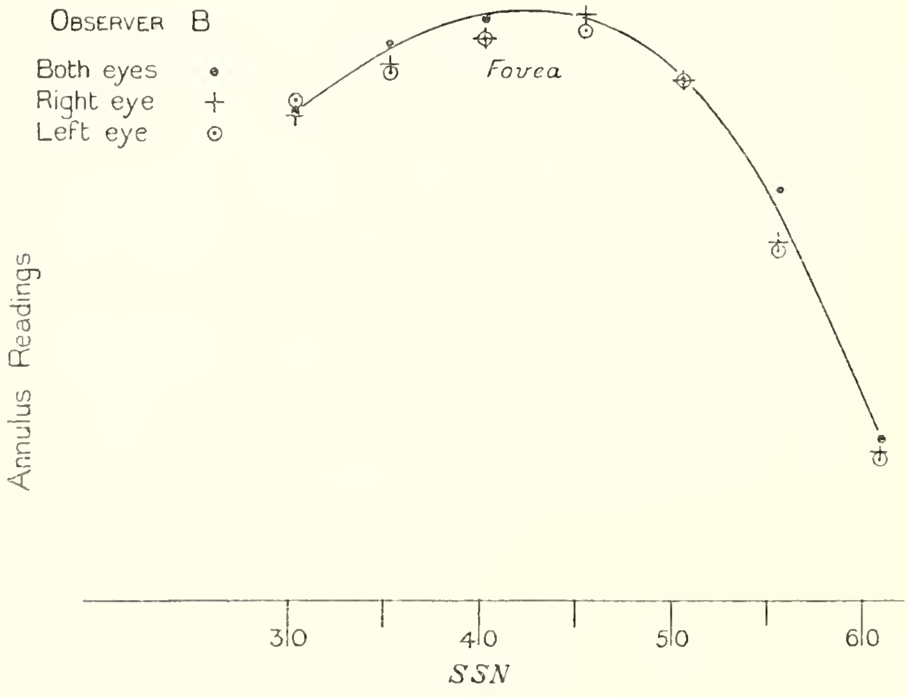

Fig. 14.

readings for the left eye are decidedly lower (a lower annulus reading corresponds to a higher threshold value) than for the right eye. Further, that with the two eyes together the threshold values agree with those corresponding to the better of the two eyes taken alone. At the fovea the threshold values are the same whether both eyes are used or either eye separately. In the case of B., figs. 14, 15, the values obtained with each eye separately agree with the values obtained with both eyes used together. These experiments are at variance with those of Piper, and show that for a typical observer of either class and for an object subtending an angle of 34 minutes and using momentary stimuli there is no evidence of binocular summation. Whether the difference can be accounted for by retinal fatigue, where as in Piper's experiments the light was kept on continuously, must be left for further experimental investigation.

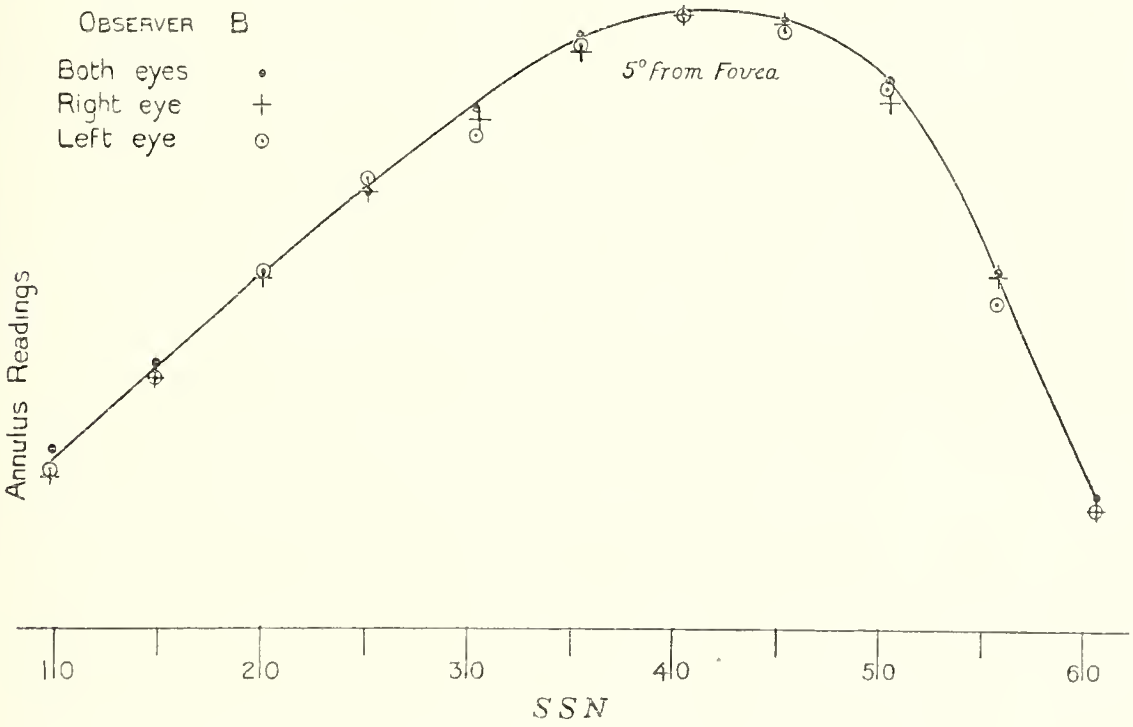

Fig. 15.

Another point which has been examined is the question as to the influence of the size of the stimulus light on the threshold values. In Table III. and figs. 16A and 16B are given the results obtained by W. using discs of diameters 2·8, 6·33 and 13·0 mm. which subtended at the eye angles of 14 and 31 minutes and 1 degree 2 minutes respectively. Observations were made both at the fovea and at 5 degrees from the fovea. When comparing these results with those given in Table II. it must be observed that owing to loss of accommodation during the interval which elapsed between the two sets of observations W. had to use spectacles when making these latter measurements. In the figure the logarithms of the energy at the threshold have been plotted against the logarithm of the diameter of the disc on which the stimulus light fell.

Table III.

Angle subtended by disc.		1° 8′.		34′.		17′.	
SSN.		log reduction.	log energy.	log reduction.	log energy.	log reduction.	log energy.
60	At 5° from fovea.	$\bar{1}\cdot012$	$1\cdot429$	$\bar{1}\cdot327$	$1\cdot744$	$\bar{1}\cdot795$	$2\cdot212$
55		$\bar{3}\cdot873$	$0\cdot052$	$\bar{2}\cdot308$	$0\cdot487$	$\bar{2}\cdot876$	$1\cdot055$
50		$\bar{4}\cdot848$	$\bar{2}\cdot830$	$\bar{3}\cdot333$	$\bar{1}\cdot315$	$\bar{2}\cdot031$	$0\cdot013$
45		$\bar{4}\cdot293$	$\bar{2}\cdot089$	$\bar{4}\cdot676$	$\bar{2}\cdot472$	$\bar{3}\cdot521$	$\bar{1}\cdot317$
40		$\bar{4}\cdot126$	$\bar{3}\cdot724$	$\bar{4}\cdot555$	$\bar{2}\cdot153$	$\bar{3}\cdot388$	$\bar{2}\cdot986$
35		$\bar{4}\cdot198$	$\bar{3}\cdot629$	$\bar{4}\cdot660$	$\bar{2}\cdot091$	$3\cdot531$	$\bar{2}\cdot962$
30		$\bar{4}\cdot424$	$\bar{3}\cdot677$	$\bar{4}\cdot903$	$\bar{2}\cdot156$	$\bar{3}\cdot776$	$\bar{1}\cdot029$
25		$\bar{4}\cdot761$	$3\cdot840$	$\bar{3}\cdot241$	$\bar{2}\cdot320$	$\bar{2}\cdot082$	$\bar{1}\cdot161$
20		$\bar{3}\cdot155$	$\bar{2}\cdot079$	$\bar{3}\cdot677$	$\bar{2}\cdot601$	$\bar{2}\cdot440$	$\bar{1}\cdot364$
15		$\bar{3}\cdot505$	$\bar{2}\cdot261$	$\bar{2}\cdot143$	$\bar{2}\cdot899$	$\bar{2}\cdot855$	$\bar{1}\cdot611$
10		$\bar{2}\cdot165$	$\bar{2}\cdot683$	$\bar{2}\cdot606$	$\bar{1}\cdot124$	$\bar{1}\cdot306$	$\bar{1}\cdot824$
60	At fovea.	$\bar{2}\cdot976$	$1\cdot393$	$\bar{1}\cdot129$	$1\cdot546$	$\bar{1}\cdot292$	$1\cdot709$
55		$\bar{2}\cdot246$	$0\cdot425$	$\bar{2}\cdot429$	$0\cdot608$	$\bar{2}\cdot574$	$0\cdot753$
50		$\bar{2}\cdot130$	$0\cdot112$	$\bar{2}\cdot378$	$0\cdot360$	$\bar{2}\cdot565$	$0\cdot547$
45		$\bar{2}\cdot251$	$0\cdot047$	$\bar{2}\cdot533$	$0\cdot329$	$\bar{2}\cdot788$	$0\cdot584$
40		$\bar{2}\cdot470$	$0\cdot068$	$\bar{2}\cdot800$	$0\cdot398$	$\bar{1}\cdot064$	$0\cdot662$
35		$\bar{2}\cdot920$	$0\cdot351$	$\bar{1}\cdot219$	$0\cdot650$	$\bar{1}\cdot505$	$0\cdot736$

A good deal of work on the influence of the size of the stimulus surface on the threshold has already been published (see Nagel in Helmholtz's 'Physiol. Optik,' 3 edit., 2, p. 284). Thus for the dark adapted eye Loeser found that for the fovea the threshold varied inversely as the square of the diameter of the circular surface used as a stimulus. For peripheral regions of the retina Piper found that the threshold varied inversely as the diameter. One of us in a previous communication ('Phil. Trans.' A, vol. 190, 168, 1897) found that for the fovea and for discs which did not subtend a greater angle than 4 degrees the threshold varied inversely as D/·65 where D is the diameter of the stimulus disc or the angle subtended at the eye. If the threshold value, T, varies inversely as D^n, then on plotting the logarithms of the threshold values against the logarithms of D we should obtain a straight line, the tangent of the inclination of which to the D axis will be equal to n. In figs. 16A and 16B dotted curves are drawn for values of n equal to 1, 1·65 and 2, that is corresponding to the results obtained by Piper, Abney, and Loeser respectively. From figs. 16A and 16B it will be seen that the numbers obtained by W. by the method described in this paper give approximately straight lines at the fovea and at the red end of the spectrum at 5 degrees from the fovea, but depart very appreciably from a straight line throughout the rest of the spectrum at 5 degrees. At the fovea the inclination of the lines joining the observed points agrees fairly closely with that corresponding to the threshold value varying inversely as the diameter. At 5 degrees on the other hand the inclination of the lines joining the observed points is approximately that corresponding to the threshold

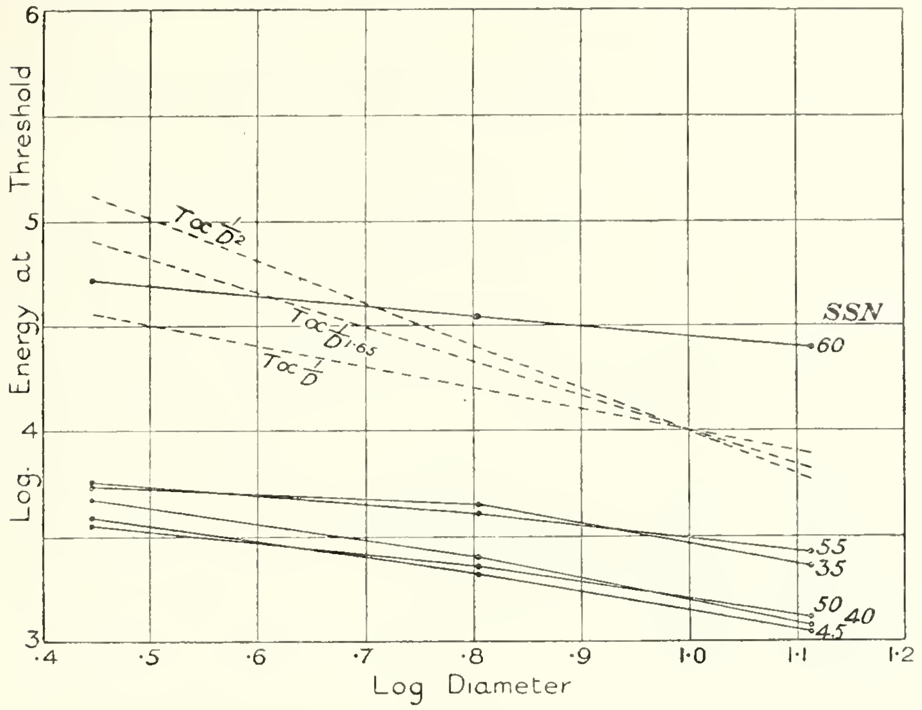

Fig. 16A.

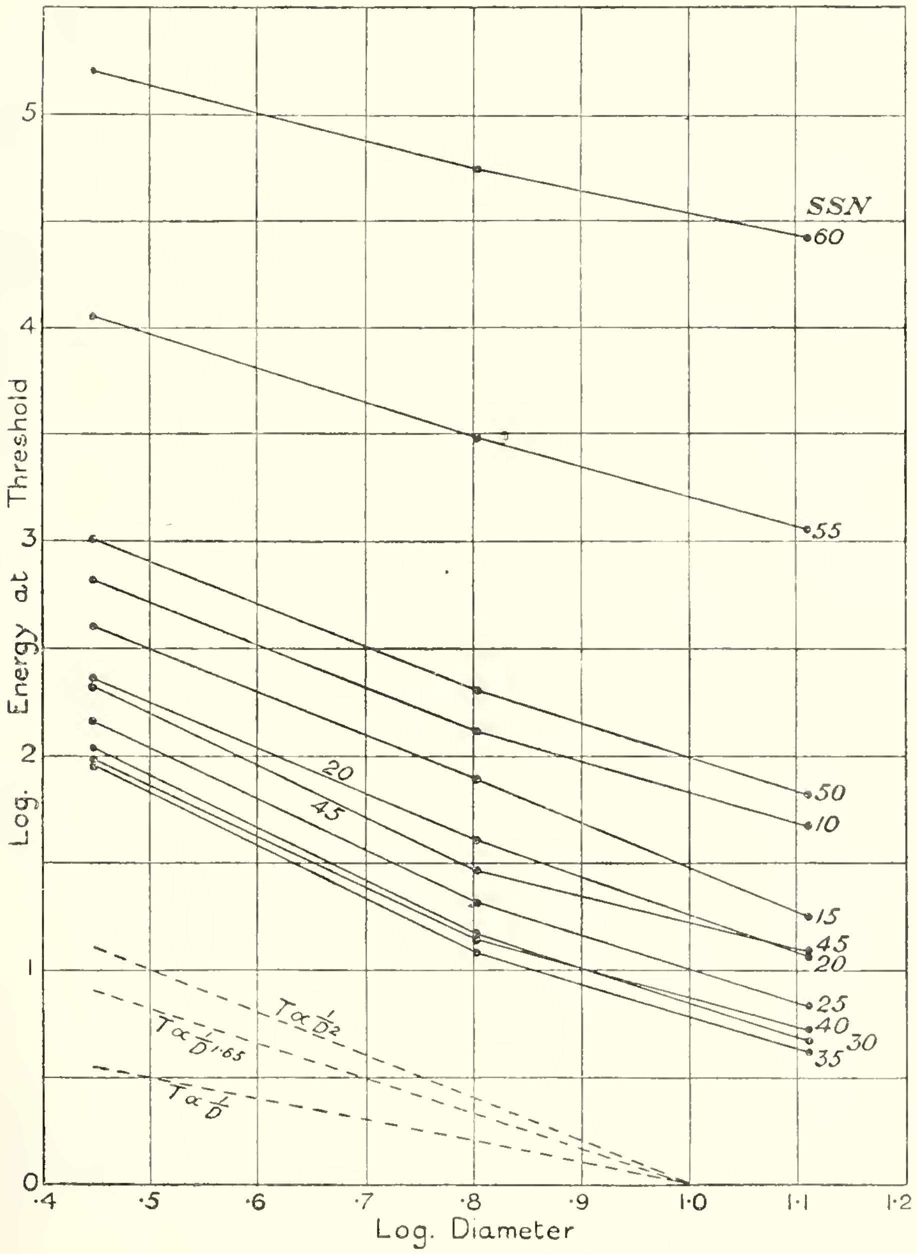

Fig. 16B.

values varying inversely as the square of the diameter. The results are therefore in marked contradiction to those obtained by LOESER and PIPER.

3. *Luminosity at the Threshold.*

In the preceding section we have considered the threshold values measured in terms of the objective energy of the radiation required to produce the sensation of light. We have now to consider what are the threshold values measured in terms of subjective light. In other words, in place of using the energy curve to give the distribution of the radiation in the spectrum, we have to use the luminosity curve, that is the curve which gives the relative brightness of the different parts of the spectrum considered as light. Now the shape of the normal luminosity curve varies with the intensity of the spectrum; the curve obtained with a bright spectrum when the cones are principally, if not exclusively, functionary, differs markedly from that obtained with a very feeble spectrum when the rods are alone operative. In the case of threshold vision we have to do with rod vision except in the red and for the foveal values obtained by observers of class I., and hence the luminosity curve to be employed to give the relative brightness of the different parts of the spectrum is that obtained at extremely low intensities or at any rate where the rods are alone operative. Such a curve can be obtained by a person having normal colour vision by the use of a very feeble spectrum but the observations are very difficult. Hence it is better to make use of the fact that the luminosity curve of a person who has monochromatic colour vision corresponds to rod vision only. One of us has determined the luminosity curves of three monochromats and we have taken the mean of the three as giving the rod luminosity curve. The observations were taken with the arc as a source of light but by means of the energy curves given in fig. 3 we have calculated the corresponding curve for the Nernst light. The values both for the arc and for the Nernst as light sources are given in Table IV.

TABLE IV.—Luminosity Curves for Monochromat (Rod Vision).

SSN.	Luminosity.		SSN.	Luminosity.	
	Arc.	Nernst.		Arc.	Nernst.
52	8·8	14·2	30	42·2	37·5
50	19·2	28·1	28	32·1	27·5
48	35·5	47·9	26	24·4	20·4
46	56·4	71·4	24	18·6	15·1
44	74·5	88·0	22	13·7	11·1
42	86·1	95·3	20	10·1	8·1
40	87·8	93·8	18	8·1	6·4
38	84·8	86·0	16	5·9	4·6
36	78·8	78·0	14	4·7	3·6
34	69·3	66·2	12	3·2	1·6
32	56·5	51·5	10	2·3	

In the case of foveal vision for observers of class I. we have to do with cone vision and hence the luminosity curve to be employed is that corresponding to a bright spectrum. In Table V. are given the values of the luminosity obtained by W. with a bright spectrum and with the Nernst light as a source.

TABLE V.—Luminosity Curve, Bright Spectrum (Cone Vision) for W. Source of Light, Nernst Glower.

SSN.	Luminosity.	SSN.	Luminosity.
62	3·0	44	75·0
60	11·5	42	59·5
58	27·0	40	42·5
56	56·0	38	27·5
54	83·0	36	15·2
52	94·5	34	8·2
50	99·5	32	4·7
48	99·0	30	4·5
46	90·0	28	4·0

If we multiply the extinctions (that is the reductions of the various parts of the spectrum to give the threshold) by the corresponding luminosities, the products will give us numbers which are proportional to the amounts by which the different colours of the spectrum must be reduced to give the threshold. This supposes each colour before reduction to be equally bright.*

In fig. 17 are given the foveal curves for the observers of class I., the ordinates being the product of extinction into cone luminosity. The curves are rather irregular, but it must be remembered that in the case of observers of this class the foveal observations are very much more difficult to obtain than extrafoveal values. If we take the mean of all the observations the product of extinction into luminosity is very nearly constant except in the neighbourhood of SSN 40 ($527 \mu\mu$), where there is a decided rise. It is, however, to be remarked that this point in the spectrum appears to be the most difficult to obtain good central fixation, and W., who has had much more experience in making these observations than any of the others, does not obtain a high value at this point. On the whole we think we may conclude that for class I. at the fovea the threshold values throughout have the same fraction of the original brightness; this original brightness being the same for all colours.

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* With class I. before reduction each colour produces an equal sensation by means of cones only with foveal fixation or with the rods also for foveal vision with class II., and for extra-foveal vision for both classes.

In fig. 18 are given the foveal extinctions for the observers of class II. multiplied by the rod luminosities. Except in the orange and red, where we have chiefly to do with cone vision, the curve for observer B. is a horizontal straight line, showing that throughout this region the threshold values correspond to equal brightnesses as far as rod vision is concerned. For observer A. the curve rises steadily from the yellow to the violet. This rise is probably due to a slight colouration of the lens, which is indicated also by other measurements. Owing to this colouration the values assumed for the luminosity are too high for A. In the case of Ar. we seem to have a curve intermediate in character between those corresponding to the two classes. It has a well-marked maximum at SSN 45.

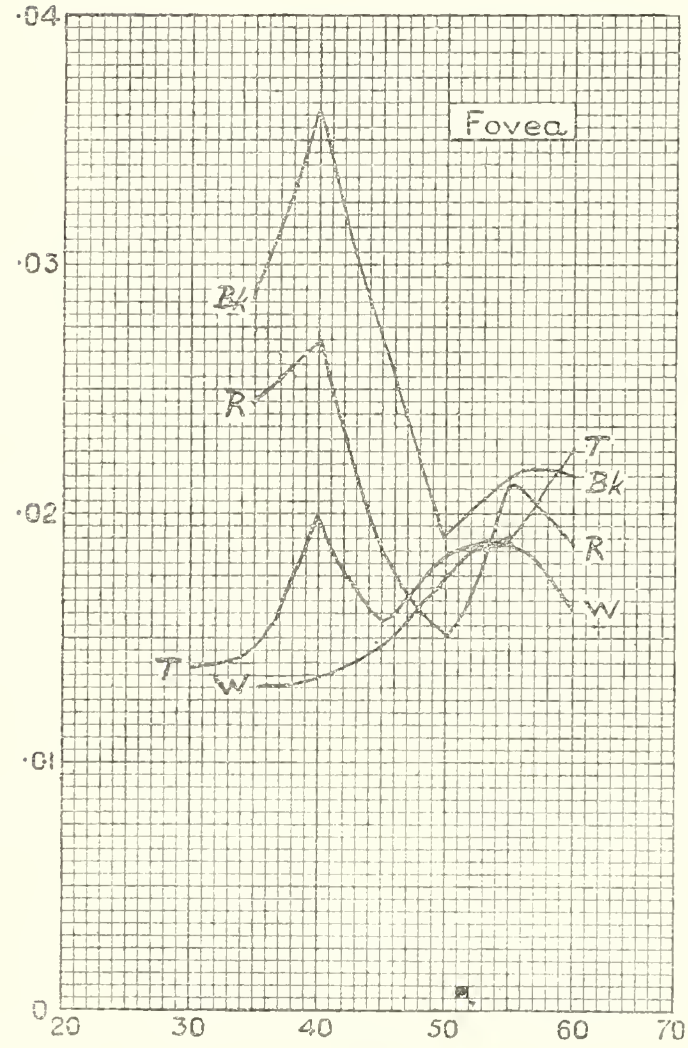


Fig. 17.

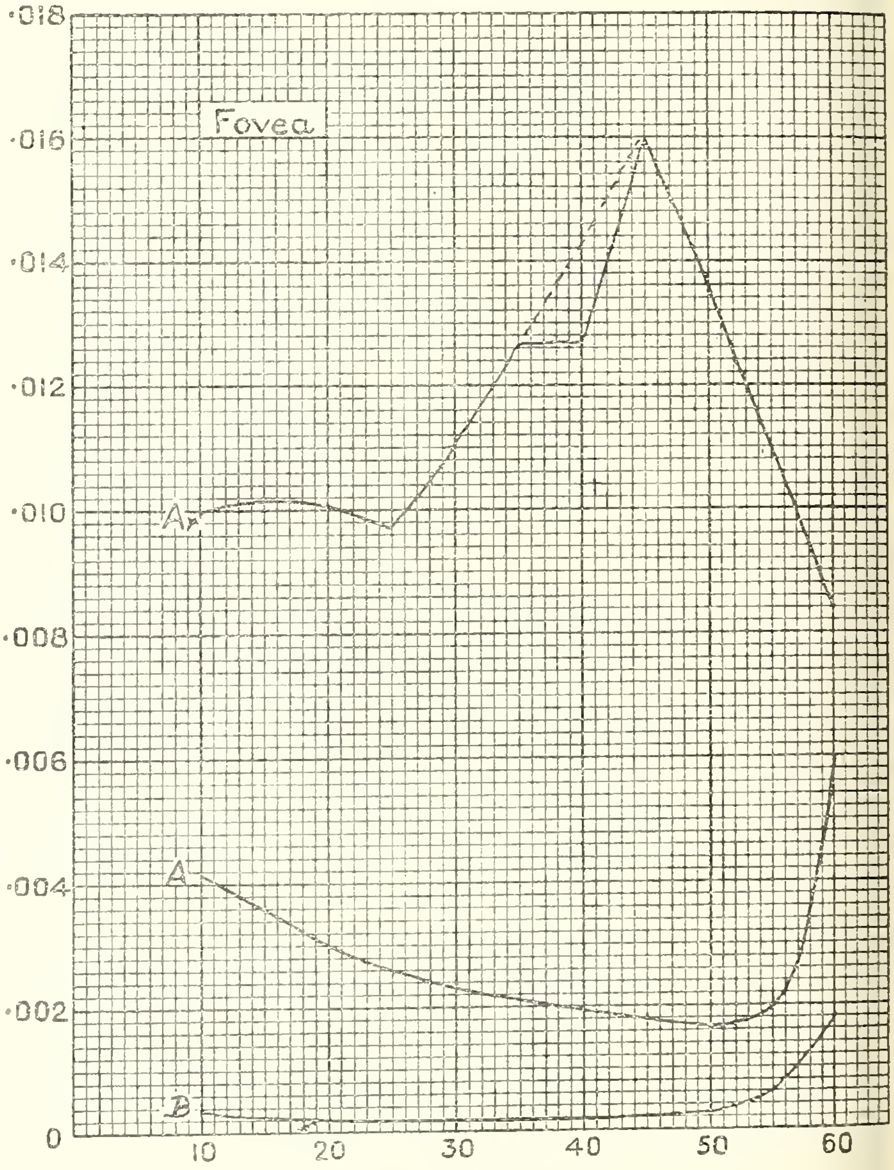
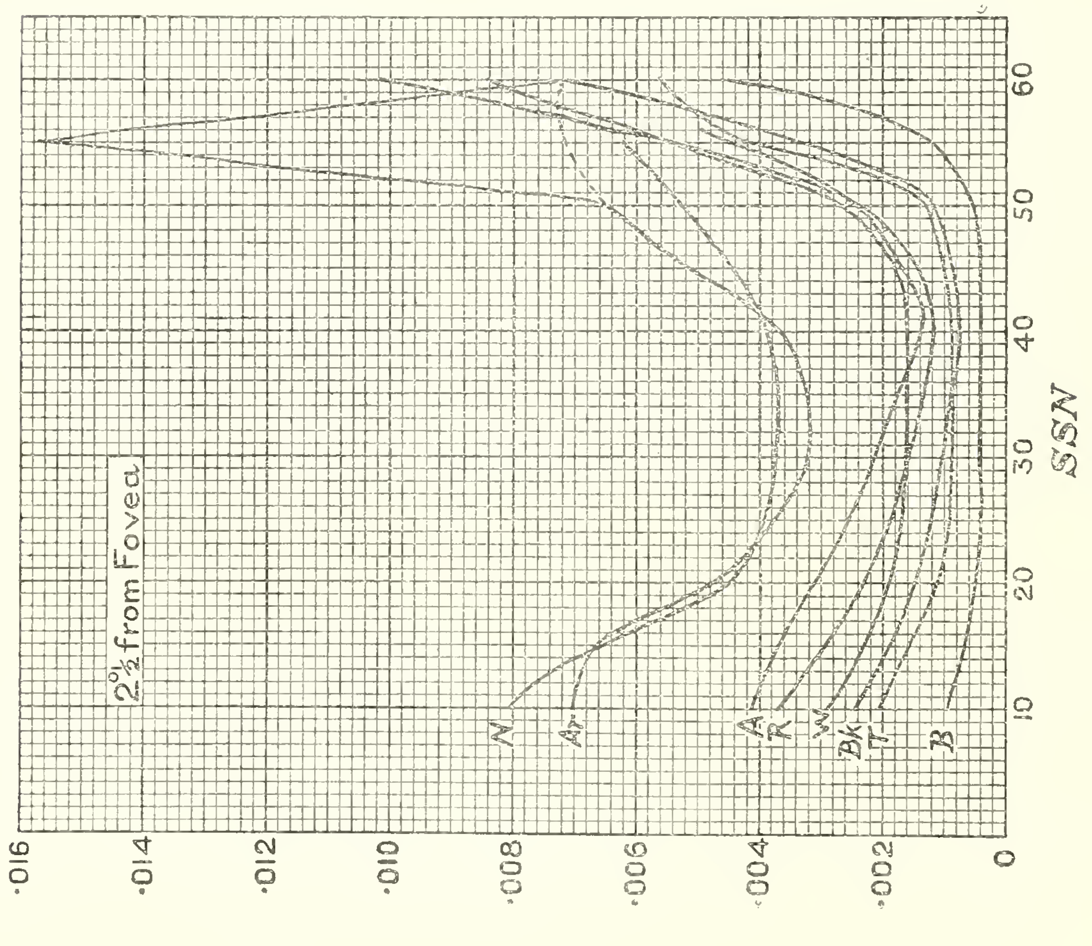


Fig. 18.

At 1·25 degrees from the fovea the results for the observers of class I. obtained by using the rod luminosity curve approximate in the case of three observers to those of class II., fig. 19. In the case of R. and W. there is a marked rise at the violet end of the spectrum. Of the observers of class II., A. and B. have nearly horizontal curves throughout the greater part of the spectrum, while AR.'s curve rises markedly towards the violet end, here again resembling the values obtained by class I.

Fig. 19.

At 2·5 degrees, 5 degrees, and 10 degrees from the fovea, as shown in figs. 20, 21, and 22, the results obtained by the two classes resemble one another, and, except at the red end of the spectrum, the product of the extinction into the rod luminosity is nearly constant. There is in the case of some observers a tendency for the product to increase towards the violet, but it must be remembered that the luminosity


2½° from Fovea
N
Ar
A
R
W
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T
B
·016
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40
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60
SSN

Fig. 20.

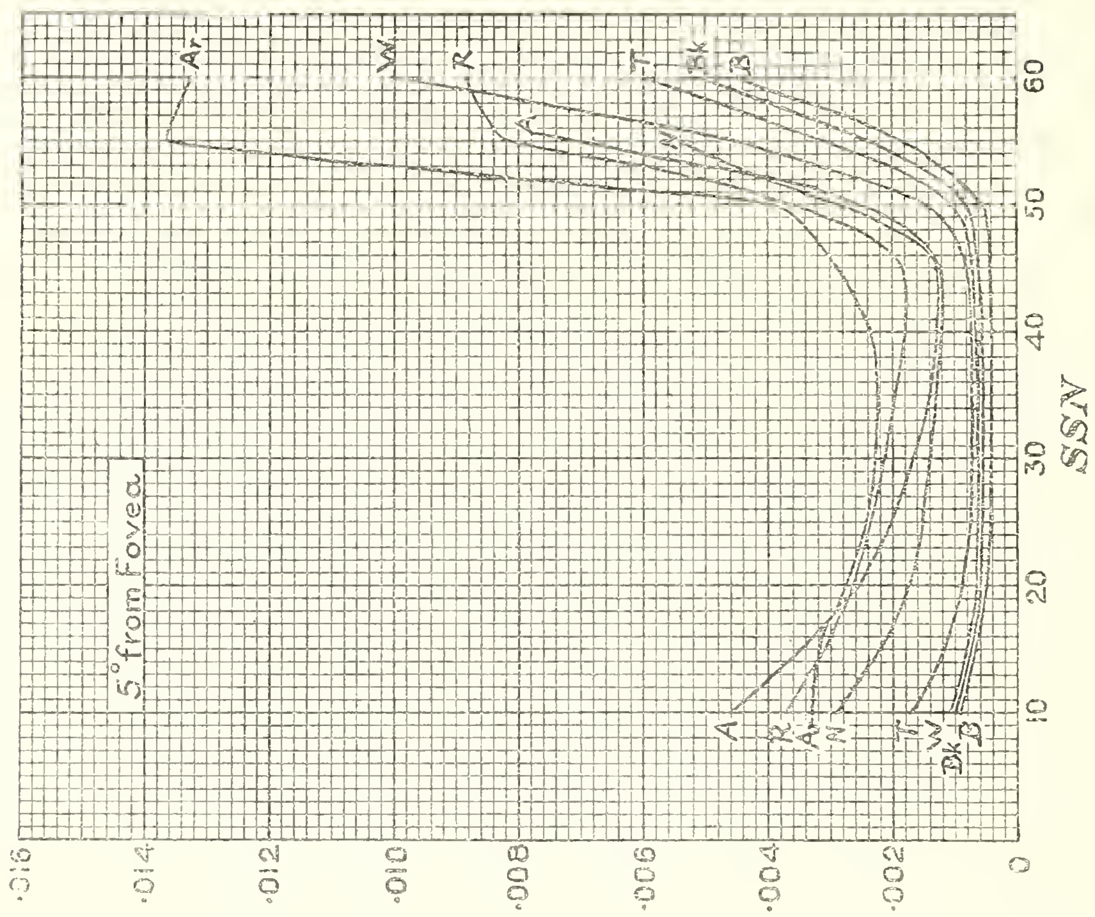
5° from Fovea
Ar
W
R
T
Bk
B
A
N
A
R
Ar
N
T
W
Bk
B
·016
·014
·012
·010
·008
·006
·004
·002
0
10
20
30
40
50
60
SSN

Fig. 21.

measurements in this region are more uncertain than in the brighter parts of the spectrum. Differences in the absorption values of the eye-media are also most likely to have the greatest effect in this region.

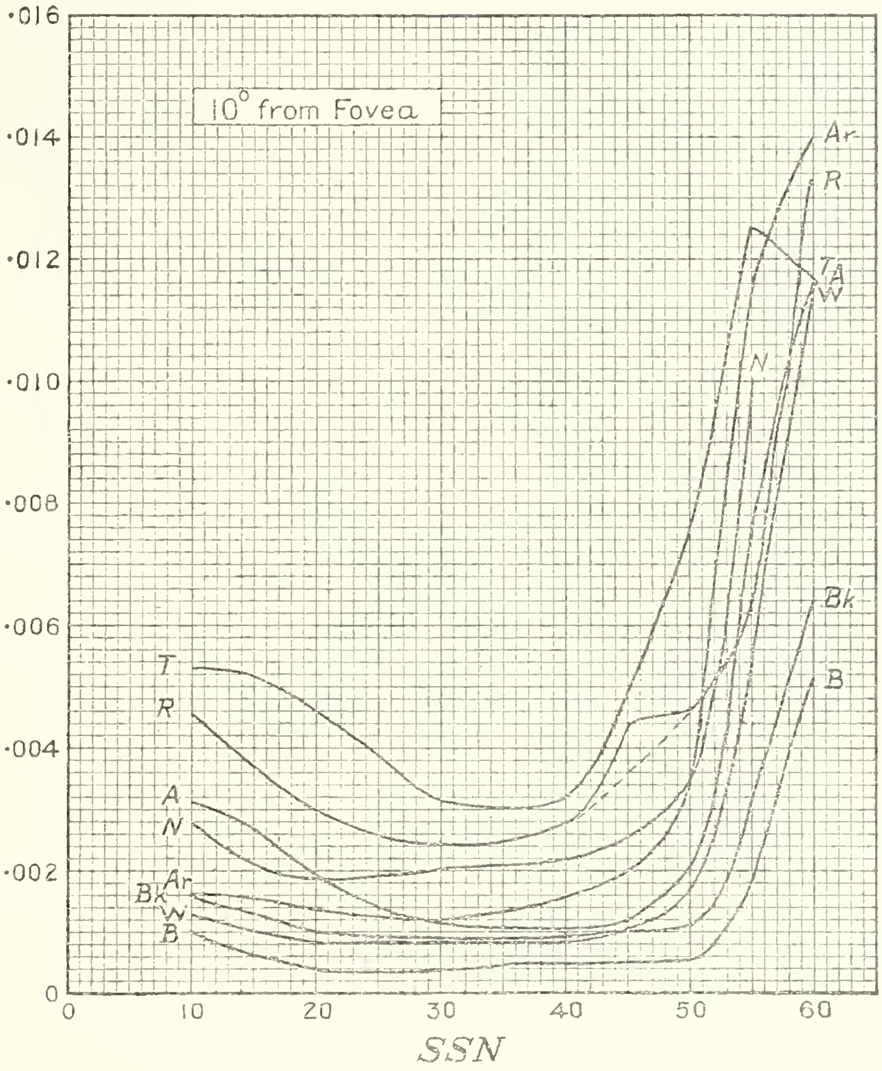

Fig. 22.

. 4. *Method of Examining the Distribution of Rods in the Retina.*

The determination of the threshold values for foveal fixation, as described above, enables us at once to say whether an observer belongs to class A. or to class B. Since, however, it takes a considerable time to obtain a set of observations, as it is necessary to go on taking sets till it is quite certain that correct foveal fixation is being obtained, examining any number of persons by this method is a very lengthy process. Hence we have devised another method which enables one in a few minutes to settle to which class an observer belongs.

By means of a plane mirror, M, fig. 23, to which is imparted an oscillatory motion about a vertical axis, the light passing through the slit, C, attached to a slide, AB, which is in the plane of the spectrum, is reflected on to a white screen, HJ. By means of a diaphragm placed against the first face of the prism train of the colour patch apparatus, a spot of light having a diameter of 12 mm. is formed on the screen. At the middle, K, of the screen are pierced two pinholes, one vertically over the other and 1 inch apart. Behind these holes is placed a lamp, L, and a piece of red glass, N. These holes provide fixation points for the observer, who is placed at P at a distance of 1 metre from the screen. The wheel, G, is driven by an electric motor at such a speed that the spot makes one complete to-and-fro vibration in 1·4 seconds, the amplitude of the motion being so great that the spot passes completely off the screen at each end of its travel. In its passage across the screen the spot passes half-way between the pinholes. The slit, C, is opened by means of a micrometer screw so that the brightness of the spot of light can be adjusted. If the slit is placed at SSN 40 ($527\mu\mu$) and the spot is bright, an observer of class I., who keeps his eye fixed half-way between the two fixation spots, sees a band of light across the screen each time the spot crosses. This band of light appears dark green at the centre and a much lighter green and brighter at the sides. As the intensity of the light is reduced the centre becomes a darker and duller green while the sides remain bright but lose their colour. Finally an intensity is reached when no light at all is seen at the centre although the sides are quite bright. It is interesting to notice how very well marked is the centre area over which the sensation of light is not perceived, this area corresponding of course to the rod-free region of the retina.

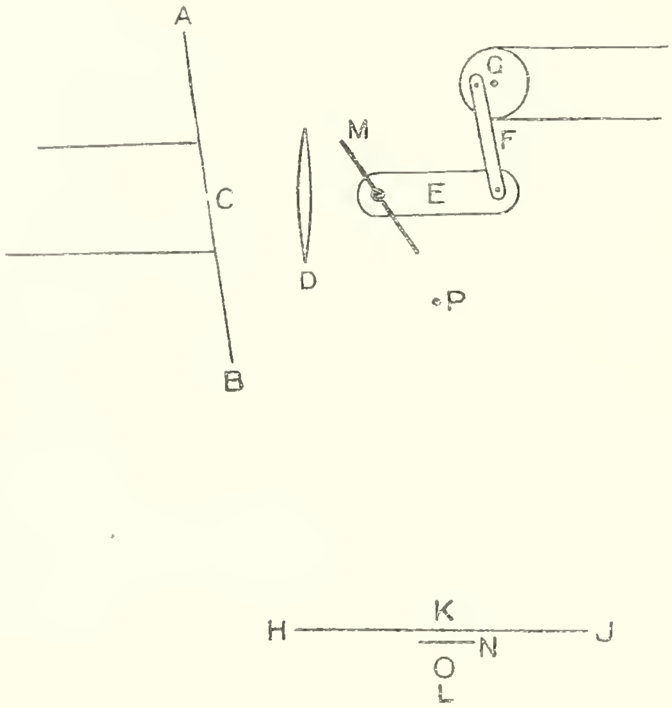

Fig. 23.

If the same series of changes is repeated with an observer of class II., the results obtained are quite different. At fairly high intensities there seems little difference between the centre and the sides in colour, though the centre generally seems slightly less bright. When the intensity of the light is reduced to such an extent that to an observer of class I. there is no sensation of light in the centre, an observer of class II. sees a continuous streak of light, the brightness at the centre being little less than that at the sides. If the intensity is reduced to about one-twentieth of that required for central extinction for class I., the centre also appears dark for class II., but the sides then are very faint, in fact the threshold is almost reached throughout.

If a red (SSN 50, $632\mu\mu$) spot of light is used, then for both classes the streak of light looks brighter at the centre than at the sides, whatever the intensity.

The explanation of these results is that with the green light, which stimulates both the rods and the cones if sufficiently bright, when the intensity is reduced below the cone threshold in the case of class I. (where there are no rods at the fovea), no sensation is produced in this region. In the periphery, where there are rods, the stimulus is sufficient to cause the sensation of light. In the case of class II., since there are rods at the fovea, the stimulus even when below the cone threshold is sufficient to cause a sensation of light by means of these rods. With a red light, since this colour is unable to stimulate the rods, we have only to do with cone vision, and the results obtained indicate that the cone sensation is a maximum at the fovea for observers of both classes. By means of this apparatus we have tested ten persons, and as a result find that eight of them belong to class I. and two to class II.

This method of examining, in which there is no difficulty in obtaining correct fixation, may perhaps be of considerable assistance to ophthalmologists when examining a central scotoma.

It is rather curious that when one of us (A.) made the investigation as to the sensitiveness of the retina described in a previous communication ('Phil. Trans.,' A, vol. 190, p. 155, 1897) he confirmed his results by means of those obtained by B., and as they agreed, he concluded that the results obtained applied to all normal eyes. We now know that both A. and B. belong to a class which seems to form only a small proportion of normal eyes.

There has been some considerable discussion whether the secondary image or BIDWELL's ghost which is seen to follow a moving spot of light when the eye is kept stationary occurs at the fovea. Using the arrangement described above, but causing the spot of light to travel much more closely, we have examined this question in the case of a typical observer of each class. Using a green stimulus light the ghost is very well marked, and to W., an observer of the first class, the ghost always appears to jump the fovea. In the case of an observer of the second class, B., the ghost is seen to follow the primary right across the field, no interruption at the fovea taking place. It would thus appear that the rods and not the cones are involved in the production of this secondary image.*

* [When this was in print we were not aware of McDOUGAL's experiments on the Bidwell ghost. His paper should be examined in connection with the results given in the above paragraph.—*October 20, 1915.*]

5. *Visibility of Radiation.*

Having determined the energy distribution for the two sources of light we have employed, it seemed of interest to obtain the visibility that is the quotient of the luminosity by the energy throughout the spectrum. We have done this in the case of the observer W. (who has no rods at his fovea), taking care to use, when making the luminosity measurements, a photometer field of such a size that the image formed on the retina was confined to the fovea. The luminosity values obtained are given in Table V. and the corresponding visibilities are plotted in fig. 24, the values obtained with the arc light being shown by the continuous line and those with the Nernst by the dotted curve. The two curves are in very fair agreement except on the blue side of the maximum, a region of the spectrum where it is always difficult to make concordant measurements of luminosity by the equality of brightness method which was employed in this case. These results, together with those obtained by previous workers, are shown in fig. 25, where the mean of the values obtained with the arc and Nernst instruments are shown by the full line curve. Nutting[*] and Ives[†] both used the flicker method of measuring the luminosity. Nutting measured the energy distribution directly, while Ives calculated it from the energy distribution in the source as obtained by other observers and the measured

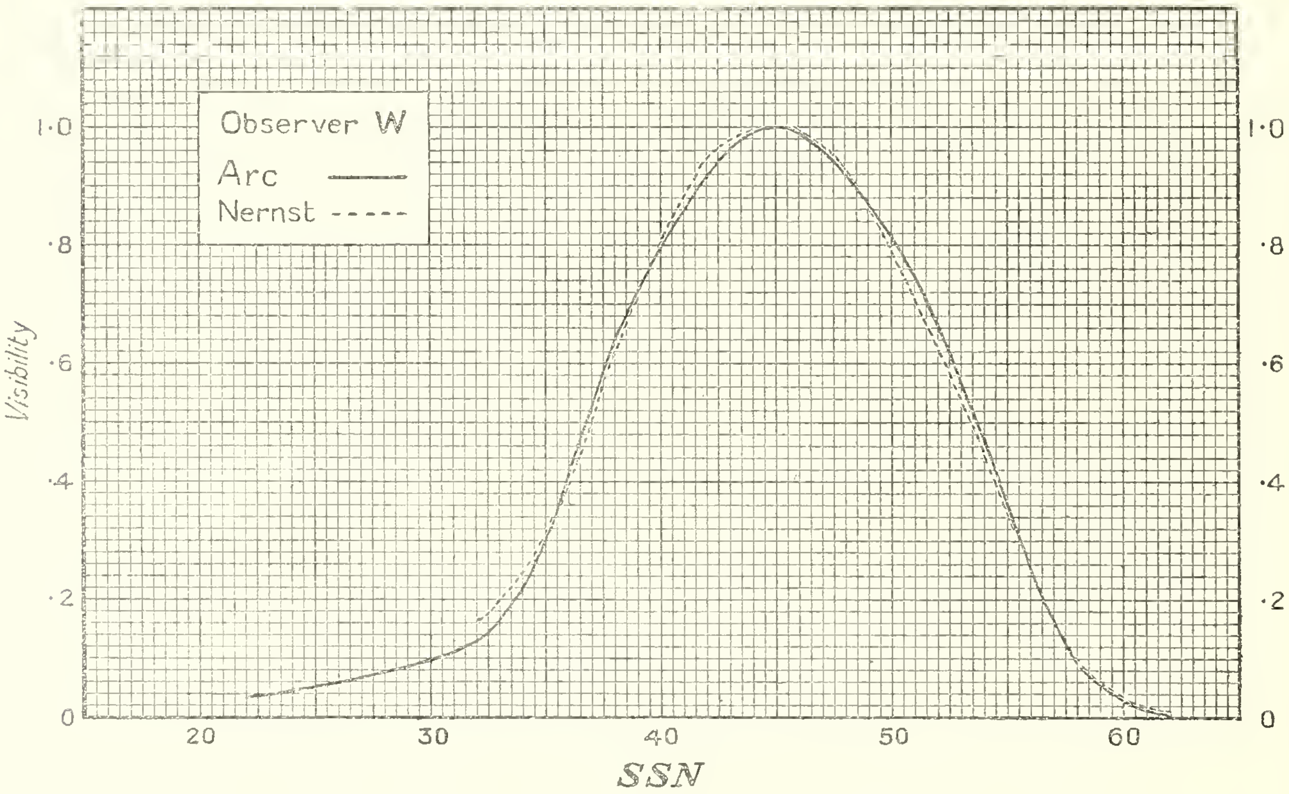

Fig. 24.

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[*] 'Phil. Mag.,' p. 304, Feb., 1915.

[†] 'Phil. Mag.,' p. 859, Dec., 1912.

dispersion and absorption of his instrument. KOENIG's[*] values given are those recalculated by NUTTING, and in this case also the energy distribution was not directly[†] measured. HOUSTON's[‡] values are the mean of those obtained by a number of observers and the energy was again calculated. It is fairly evident that in this case some serious error has been made in determining the energy distribution. At first sight it looks as if the intensity of the spectrum used by HOUSTON was so low that he was dealing mainly with rod vision. That this is not the true explanation is shown by the fact that he also publishes results obtained with a much less intense spectrum, and the maximum he obtains for this rod visibility curve is as much below the value obtained by other observers for the rod curve as is the maximum he obtains for the bright or cone visibility curve.[§] Our curve lies considerably below those obtained by other observers in the blue and violet. This is probably almost entirely due to the fact that we are dealing with pure cone vision, while other observers, who apparently used a much larger photometric field, were probably dealing with a mixed

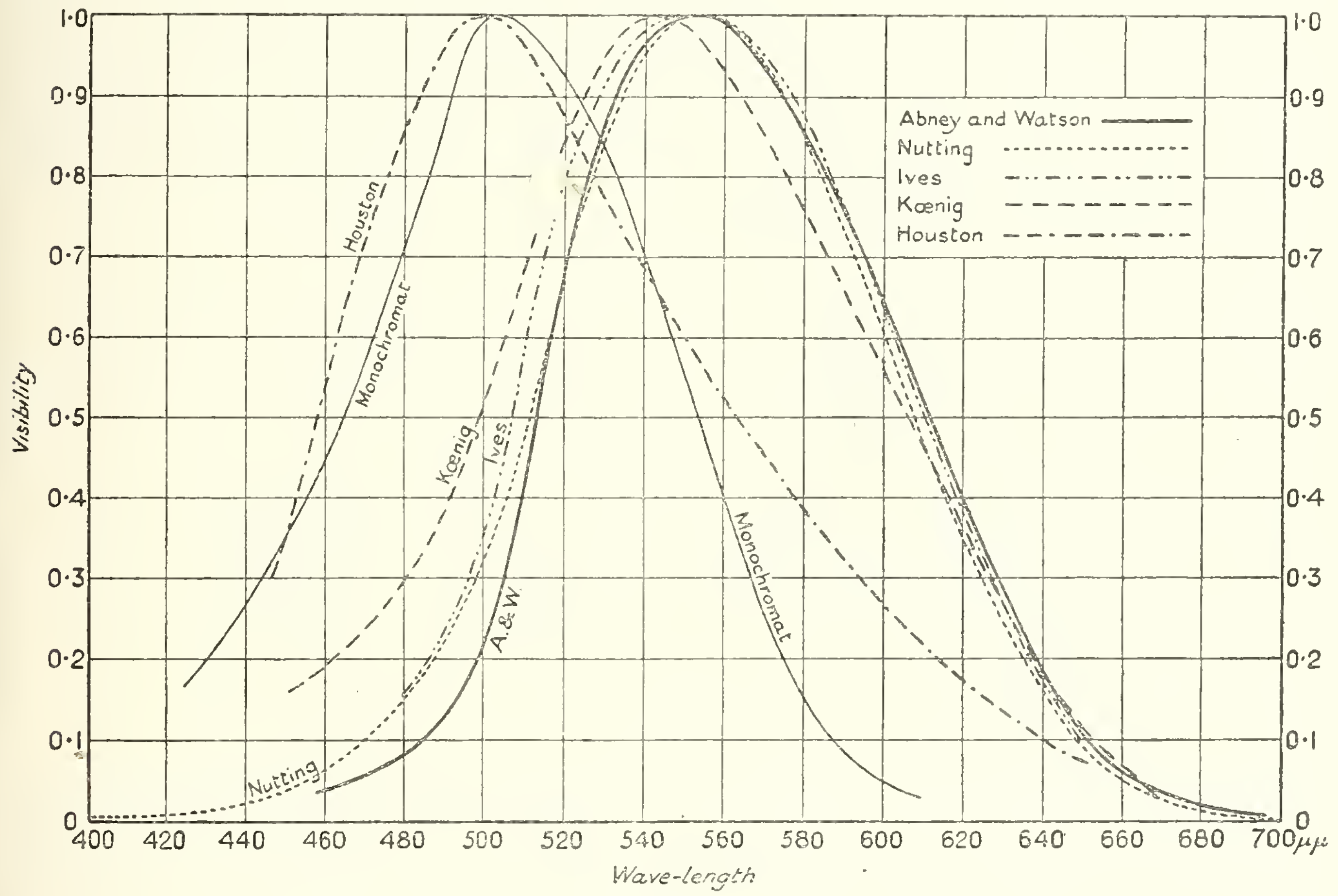

Fig. 25.

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[*] 'Bull. Bureau of Standards,' 7, 238, 1911.

[†] 'Phil. Mag.,' p. 715, May, 1913.

[‡] The calculations of energy can only be considered as close approximations of the radiation from perfectly black bodies. If not black deviation from absolute measurement of energy is to be expected.

[§] Displaced from the mean of all the other observers.

rod and cone sensation which would increase the luminosity values in the blue and violet.

Using the luminosity values given in Table IV. for rod vision, as deduced from experiments on monochromats, we have calculated the corresponding visibility curve and it is shown in fig. 25.

6. *Relative Sensitiveness of the Foveal and Parafoveal Regions.*

Observer W., with a rodless fovea, made a series of measurements of the relative intensities of two lights, one of which falls on the fovea and the other on the parafoveal region, when the sensations produced are the same, that is when the two lights appear equally bright. In this way we compare the sensitiveness of a part of the retina where there are only cones with that of a region where there are both rods and cones, and by making this comparison at different intensities of the stimulus light we obtain an insight as to the manner in which the relative sensitiveness of the rods and cones varies with the intensity.

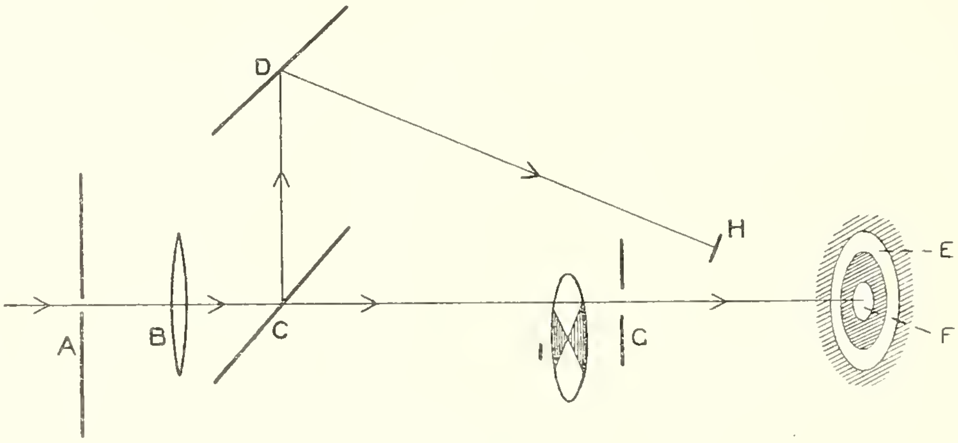

Fig. 26.

The arrangement employed is shown diagrammatically in fig. 26. The light of the required colour passes through a slit, A, attached to the slide of the spectrum apparatus, and a lens, B, is so adjusted as to give an image of the first face of the prism train on the screen, EF. The light passes through a sheet of plane glass, C, placed at 45 degrees, and the part of the light reflected from this glass is again reflected from a silvered mirror, D, on to the screen. This screen consists of a central white disc, F, of such a size that its radius subtends an angle of 43 minutes at the observer's eye and a circular annulus, E, of which the radius of the inner edge subtends an angle of 2 degrees at the observer's eye and that of the outer edge 3 degrees. The space between the central disc and the annulus is painted dead black. A diaphragm, G, is so arranged that the light which passes straight through the glass plate, C, only illuminates the disc, F; while an opaque disc, H, screens this central disc from the light, which has been reflected from the mirrors C and D, so that this light only illuminates the annulus, E. A set of adjustable sectors, I, placed in the path of the light which illuminates the disc, allows of the intensity of the illumination being adjusted. By removing H and placing a rod so as to form a Rumford photometer, the intensity of the beam which goes straight through and is doubly reflected, respectively, can be compared. The experiment consists in adjusting the sectors so that when the eyes are kept fixed on the centre of the disc the disc and the annulus appear equally bright. Settings were taken alternately starting with the centre too bright and then too feeble. Observations were made throughout the spectrum with different intensities.*

Two series of measurements were made, one with the eye thoroughly dark adapted, the annulus being surrounded with black velvet and all stray light screened off. In the other set the eye was light adapted, a sheet of white blotting paper surrounding the annulus, and was illuminated by the white light of the arc. A screen was so placed that none of this white light fell on the annulus or disc. The intensity of the white light on the background was 1·5 lux, and was adjusted so that when a red and a blue light were compared by a person who has rods at the fovea the relative intensity of the two lights did not appear to alter, as the intensity of both was reduced in the same proportion, that is till the so-called Purkinje effect vanished.

A series of measurements were first made using a constant slit width throughout the spectrum by both W. and B., and the results are given in Table VI. and

TABLE VI.

Colour. SSN.	$\mu\mu$.	Ratio of central to parafoveal illumination for equal brightness. Dark adapted eye.	
		W.	B.
58·7	658	1·14	1·05
56·0	632	1·17	
53·3	609	1·23	1·06
50·8	589	1·29	
48·6	576	1·15	1·16
45·4	556	1·32	
42·8	541	1·38	1·10
40·1	527	1·54	
37·6	514	1·70	1·15
35·0	503	2·42	
32·2	493	4·63	1·12
27·0	474	9·53	1·32
21·8	457	13·6	1·24
16·5	442	19·6	1·34
11·2	427	23·9	1·41
5·9	415	27·0	1·49
0·7	403	27·0	1·94

---

* The slit, A, could be varied in width, the actual intensity when the slit was placed at the D line being determined by comparison with a Hefner lamp.

fig. 27. It will be observed that the two observers, one of whom belongs to class I. and the other to class II., get entirely different results. In the case of B., the ratio of the foveal to the parafoveal intensities for equal brightness does not differ greatly from unity and is very nearly constant throughout the spectrum, showing that the sensitiveness of the retina at the fovea and at 2·5 degrees from the fovea is nearly the same, a result which is confirmed by the threshold measurements. In the case of W. there is a very marked increase in the sensitiveness at 2·5 degrees as we go towards the violet, so that at SSN 5·9 (400 $\mu\mu$) the central illumination has to be 27 times the brightness of the peripheral for the brightness to appear the same. Observer A. obtains similar results to those obtained by B., except that his ratio is slightly higher at SSN 30; the maximum value of the ratio is, however, only 2. B. also made observations using a lens to view the illuminated surfaces which caused the image of the edge of the annulus to fall at 6·5 degrees from the fovea. The ratio was again practically constant, the maximum value being 1·29 at SSN 6.

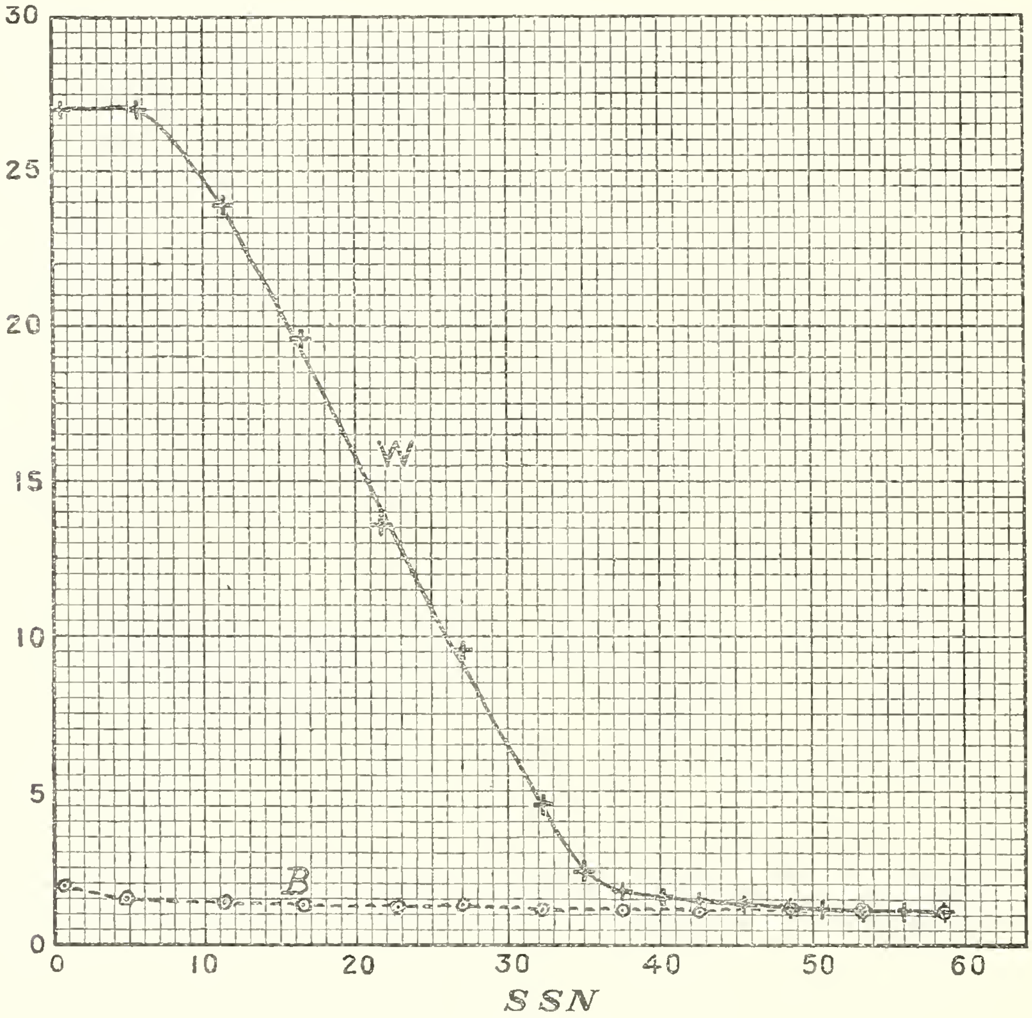

Fig. 27.

In the above series only a single intensity was used for each colour, and W. then made sets of observations with different intensities in order to study the manner in which the relative sensitiveness varies with intensity. The results obtained are contained in Table VII. With the light adapted eye it was found that the ratio was independent of the intensity so only the mean values are entered in the table. As the intensity of the illumination is increased from a very low value, the ratio of the central to the parafoveal illumination for equal brightness at first decreases rapidly, but as the intensity increases the change becomes slower and slower. Finally, for the higher illuminations, the ratio becomes practically constant and approximates to the value obtained with the light adapted eye.

Table VII.

Colour.		Intensity of peripheral illumination in terms of—	Ratio of central to peripheral illumination for equal brightness.	
SSN.	$\mu\mu$.	Luminosity (lux).	Dark adapted.	Light adapted.
53·3	609	0·027	1·93	1·07
		0·10	1·67	
		0·20	1·70	
		0·40	1·42	
		0·79	1·47	
		1·85	1·17	
		2·28	1·09	
48·6	576	0·037	2·98	0·99
		0·14	2·20	
		0·26	1·83	
		0·54	1·42	
		1·07	1·38	
		2·51	0·96	
		3·08	1·02	
42·8	541	0·11	2·64	1·04
		0·21	2·00	
		0·42	1·58	
		0·85	1·41	
		1·98	1·24	
		2·44	1·29	
		4·94	1·21	
37·6	514	0·049	4·05	1·13
		0·10	2·82	
		0·20	2·28	
		0·38	1·74	
		0·78	1·44	
		0·90	1·52	
		1·11	1·39	
		1·81	1·22	
		2·24	1·33	

TABLE VII. (continued).

Colour.		Intensity of peripheral illumination in terms of—	Ratio of central to peripheral illumination for equal brightness.	
SSN.	μμ.	Luminosity (lux).	Dark adapted.	Light adapted.
32·2	493	0·012	5·35	1·45
		0·024	5·44	
		0·05	3·81	
		0·10	3·12	
		0·21	2·39	
		0·46	2·07	
		0·58	2·06	
		0·93	1·85	
21·8	457	0·0013	9·30	1·51
		0·005	13·0	
		0·010	7·11	
		0·022	3·76	
		0·030	3·88	
		0·041	2·80	
		0·060	2·33	
		0·093	2·13	
		0·13	2·06	
		0·20	1·95	
		0·25	1·87	

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IV. *On Certain Linear Differential Equations of Astronomical Interest.*

By Prof. H. F. BAKER, *F.R.S.*

Received May 13,—Read June 17, 1915.

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PART I.

PART II.

PART III.

[Published January 5, 1916.

PREFACE.

PART II. of the present paper was written, very much in the form in which it is now presented, in the summer of 1913, and began with the remark in § 11, which appears to disprove a statement made by POINCARÉ in regard to the convergence of an astronomical series. It was laid aside partly because a good deal of the work is only of the nature of elementary algebra, partly because the matrix notation employed does not seem to find favour in its application to differential equations. Various circumstances have, however, led me to take up the matter again, and my original conviction that the method of Part II. is of importance has been strengthened by comparing it with the less formal methods which, for the sake of introducing the subject, I have followed in Part I. I hope, therefore, that the following exposition may be thought worth while. Part III. has only the value of a concluding remark.

The table of contents above may serve to give an idea of the scope and arrangement of the paper.

PART I.

§ 1. Consider a linear differential equation

$$U\frac{d^2X}{d\tau^2}+V\frac{dX}{d\tau}+WX=0,$$

where U, V, W are power series in a small quantity, λ, of the forms

$$\begin{aligned}U &= u+\lambda u_1+\lambda^2 u_2+\ldots,\\ V &= v+\lambda v_1+\lambda^2 v_2+\ldots,\\ W &= \qquad \lambda w_1+\lambda^2 w_2+\ldots,\end{aligned}$$

in which each of u_r, v_r, w_r is a linear function of

$$\zeta^r,\ \zeta^{r-2},\ \zeta^{r-4},\ \ldots,\ \zeta^{4-r},\ \zeta^{2-r},\ \zeta^{-r},$$

ζ denoting e^τ. Thus each of u_{2n}, v_{2n}, w_{2n} will contain a term independent of ζ; we speak of these as the absolute terms. It is important that W contains no term in λ^0; and it is assumed that the quantity v/u, which is independent of ζ, is not a positive or negative integer, and that u, v are not both zero.

We prove that if the absolute terms in W, that is the absolute terms in

$$w_2,\ w_4,\ w_6,\ \ldots,$$

be suitably determined, the differential equation possesses a solution of the form

$$X = 1+\lambda\phi_1+\lambda^2\phi_2+\ldots,$$

wherein ϕ_r is a linear function of $\zeta^r, \zeta^{r-2}, \zeta^{r-4}, \ldots, \zeta^{4-r}, \zeta^{2-r}, \zeta^{-r}$, and this is a periodic solution. Its period is $2\pi i$; we can, however, if we wish, express the same result with a period 2π by writing $\tau = it$.

For the substitution of the assumed form for X requires the identity

$$(u+\Sigma\lambda^n u_n)\,\Sigma\lambda^n\phi''_n + (v+\Sigma\lambda^n v_n)\,\Sigma\lambda^n\phi'_n + \Sigma\lambda^n w_n\,(1+\Sigma\lambda^n\phi_n) = 0,$$

which, equating the coefficient of λ^n to zero, will be true if

$$\begin{aligned} u\phi''_n + u_1\phi''_{n-1} + \ldots + u_{n-1}\phi''_1 & \\ + v\phi'_n + v_1\phi'_{n-1} + \ldots + v_{n-1}\phi'_1 & \\ + w_1\phi_{n-1} + w_2\phi_{n-2} + \ldots + w_{n-1}\phi_1 + w_n &= 0. \end{aligned}$$

In particular for $n = 1$

$$u\phi''_1 + v\phi'_1 + w_1 = 0.$$

If herein we suppose

$$\phi_1 = A_1\zeta + A_{-1}\zeta^{-1}, \quad w_1 = c_1\zeta + c_{-1}\zeta^{-1},$$

u, v, c_1, c_{-1} being given constants, we obtain

$$u(A_1\zeta + A_{-1}\zeta^{-1}) + v(A_1\zeta - A_{-1}\zeta^{-1}) + c_1\zeta + c_{-1}\zeta^{-1} = 0,$$

which is satisfied by

$$A_1 = -\frac{c_1}{u+v}, \quad A_{-1} = -\frac{c_{-1}}{u-v}.$$

For $n = 2$ the condition is

$$u\phi''_2 + v\phi'_2 + u_1\phi''_1 + v_1\phi'_1 + w_1\phi_1 + w_2 = 0.$$

Writing

$$u_1 = a_1\zeta + a_{-1}\zeta^{-1}, \quad v_1 = b_1\zeta + b_{-1}\zeta^{-1}, \quad w_1 = c_1\zeta + c_{-1}\zeta^{-1}, \quad w_2 = c_2\zeta^2 + c_{-2}\zeta^{-2} + C_2,$$

and assuming a form

$$\phi_2 = A_2\zeta^2 + A_{-2}\zeta^{-2},$$

the condition becomes

$$\begin{aligned} 4u(A_2\zeta^2 + A_{-2}\zeta^{-2}) + 2v(A_2\zeta^2 - A_{-2}\zeta^{-2}) & \\ + (a_1\zeta + a_{-1}\zeta^{-1})(A_1\zeta + A_{-1}\zeta^{-1}) + (b_1\zeta + b_{-1}\zeta^{-1})(A_1\zeta - A_{-1}\zeta^{-1}) & \\ + (c_1\zeta + c_{-1}\zeta^{-1})(A_1\zeta + A_{-1}\zeta^{-1}) + c_2\zeta^2 + c_{-2}\zeta^{-2} + C_2 &= 0; \end{aligned}$$

equating the coefficients of ζ^2, ζ^{-2}, ζ^0 to zero, we obtain

$$\begin{aligned} (4u+2v)\,A_2 &= -a_1A_1 - b_1A_1 - c_1A_1 - c_2, \\ (4u-2v)\,A_{-2} &= -a_{-1}A_{-1} + b_{-1}A_{-1} - c_{-1}A_{-1} - c_{-2}, \\ C_2 &= -a_1A_{-1} - a_{-1}A_1 + b_1A_{-1} - b_{-1}A_1 - c_1A_{-1} - c_{-1}A_1, \end{aligned}$$

which, as v/u is not 2 or -2, determine A_2, A_{-2}, and C_2, the last being expressible by means of the given coefficients of u, v, u_1, v_1, w_1.

Proceeding similarly with the general value of n, we at once reach the conclusion stated, the absolute term in w_n being determined in terms of the coefficients in

$$u, u_1, \ldots, u_{n-1}, \quad v, v_1, \ldots, v_{n-1}, \quad w_1, w_2, \ldots, w_{n-1}.$$

§ 2. Now consider an equation

$$A\frac{d^2x}{d\tau^2}+2B\frac{dx}{d\tau}+Cx = 0,$$

where, with $\zeta = e^{\tau}$, A, B, C have the forms

$$\begin{aligned} A &= a_0+\lambda(a_1\zeta+a_{-1}\zeta^{-1})+\lambda^2(a_2\zeta^2+a_{-2}\zeta^{-2}+a_{20})+\ldots, \\ B &= b_0+\lambda(b_1\zeta+b_{-1}\zeta^{-1})+\lambda^2(b_2\zeta^2+b_{-2}\zeta^{-2}+b_{20})+\ldots, \\ C &= c_0+\lambda(c_1\zeta+c_{-1}\zeta^{-1})+\lambda^2(c_2\zeta^2+c_{-2}\zeta^{-2}+c_{20})+\ldots, \end{aligned}$$

which are periodic functions of τ, with period $2\pi i$, capable of being arranged as power series in a parameter λ, the coefficient of λ^r being a linear function of $\zeta^r, \zeta^{r-2}, \ldots, \zeta^{2-r}, \zeta^{-r}$.

In accordance with the well-known theory of linear differential equations with periodic coefficients, we substitute

$$x = e^{\kappa\tau}X,$$

where κ is a constant, and so obtain a differential equation

$$AX''+2(\kappa A+B)X'+(A\kappa^2+2B\kappa+C)X = 0,$$

which, when κ is properly chosen, is to be satisfied by a periodic function X. That this is possible follows at once from § 1, as we now explain.

First we can draw some inference as to the form of κ. For compare the original differential equation in x with the equation obtained from it by changing the sign of λ in each of the series A, B, C. It is clear that the new differential equation may equally be obtained from the original equation by change of τ into $\tau+\pi i$, which changes ζ into $-\zeta$; this latter change, however, only multiplies the factor $e^{\kappa\tau}$ by the constant $e^{i\pi\kappa}$; the factors $e^{\kappa\tau}$ appropriate to the two independent solutions of the new differential equation are thus the same, in their aggregate, as the factors for the original equation. Thus the change of the sign of λ changes the two factors $e^{\kappa\tau}$ appropriate to the two independent solutions of the original differential equation among themselves, either by leaving both unaltered or by interchanging them. Assuming that κ is capable of expression as a power series in λ,

$$\kappa = \kappa_0+\kappa_1\lambda+\kappa_2\lambda^2+\ldots,$$

the case in which each κ is unaltered by change of the sign of λ is the case in which only even powers enter in this series. The case in which the two values of κ are interchanged by change of the sign of λ may arise when the differential equation is such that for $\lambda = 0$ the two values of κ are equal or differ by an integer; in this case $e^{\kappa'\tau}/e^{\kappa\tau}$ is a periodic function for $\lambda = 0$, and the factors $e^{\kappa'\tau}$, $e^{\kappa\tau}$ do not individualise the functions with which they are associated.

In the present case, the equation reduces when $\lambda = 0$, to

$$a_0 \frac{d^2x}{d\tau^2} + 2b_0 \frac{dx}{d\tau} + c_0 x = 0,$$

which, if a_0 is not zero, has the two solutions $e^{\sigma\tau}$, $e^{\sigma'\tau}$, where σ, σ' have the values

$$[-b_0 \pm (b_0^2 - a_0 c_0)^{\frac{1}{2}}]/a_0.$$

Thus if we suppose not only that a_0 is other than zero, but also that

$$2\,(b_0^2 - a_0 c_0)^{\frac{1}{2}}/a_0$$

is not zero or a positive or negative integer, we can assume

$$\kappa = \sigma + \kappa_2 \lambda^2 + \kappa_4 \lambda^4 + \ldots.$$

Then putting

$$\mathrm{X} = 1 + \lambda \phi_1 + \lambda^2 \phi_2 + \ldots,$$

where ϕ_r is a linear function of $\zeta^r, \zeta^{r-2}, \ldots, \zeta^{2-r}, \zeta^{-r}$, the differential equation for X can be compared with that of § 1. In the present case there is an unknown quantity κ entering into the coefficient $\mathrm{A}\kappa + \mathrm{B}$ of $d\mathrm{X}/d\tau$, but it will be seen that in the equations obtained by taking the successive powers of λ, each unknown coefficient in κ in this $\mathrm{A}\kappa + \mathrm{B}$ is determined at an earlier stage as entering in the coefficient $\mathrm{A}\kappa^2 + 2\mathrm{B}\kappa + \mathrm{C}$, and so enters as a known coefficient. We have

$$\begin{aligned}
\mathrm{A}\kappa + \mathrm{B} &= [a_0 + \lambda\,(a_1\zeta + a_{-1}\zeta^{-1}) + \lambda^2\,(a_2\zeta^2 + a_{-2}\zeta^{-2} + a_{20}) + \ldots]\,[\sigma + \kappa_2\lambda^2 + \ldots] \\
&\quad + b_0 + \lambda\,(b_1\zeta + b_{-1}\zeta^{-1}) + \lambda^2\,(b_2\zeta^2 + b_{-2}\zeta^{-2} + b_{20}) + \ldots \\
&= a_0\sigma + b_0 + \lambda\,[\sigma\,(a_1\zeta + a_{-1}\zeta^{-1}) + b_1\zeta + b_{-1}\zeta^{-1}] \\
&\quad + \lambda^2\,[\sigma\,(a_2\zeta^2 + a_{-2}\zeta^{-2} + a_{20}) + a_0\kappa_2 + b_2\zeta^2 + b_{-2}\zeta^{-2} + b_{20}] \\
&\quad + \ldots,
\end{aligned}$$

and similarly,

$$\begin{aligned}
\mathrm{A}\kappa^2 + 2\mathrm{B}\kappa + \mathrm{C} &= a_0\sigma^2 + 2b_0\sigma + c_0 \\
&\quad + \lambda\,[\sigma^2\,(a_1\zeta + a_{-1}\zeta^{-1}) + 2\sigma\,(b_1\zeta + b_{-1}\zeta^{-1}) + c_1\zeta + c_{-1}\zeta^{-1}] \\
&\quad + \lambda^2\,[\sigma^2\,(a_2\zeta^2 + a_{-2}\zeta^{-2} + a_{20}) + 2\sigma\,(b_2\zeta^2 + b_{-2}\zeta^{-2} + b_{20}) + 2\kappa_2\,(a_0\sigma + b_0) \\
&\qquad + c_2\zeta^2 + c_{-2}\zeta^{-2} + c_{20}] \\
&\quad + \ldots,
\end{aligned}$$

the absolute term in the coefficient of λ^4 in this being

$$2\kappa_4(a_0\sigma+b_0)+a_0\kappa_2^2+2a_{20}\kappa_2\sigma+a_{40}\sigma^2+2b_{20}\kappa_2+2b_{40}\sigma+c_{40}.$$

Thus, as in § 1, we first put

$$a_0\sigma^2+2b_0\sigma+c_0 = 0,$$

assuming, as in § 1 it was assumed that v/u is not an integer, that

$$2(a_0\sigma+b_0)/a_0, \quad \text{or} \quad 2(a_0c_0-b_0^2)^{\frac{1}{2}}/a_0,$$

is not zero or integral; then the absolute term in the coefficient of λ^2 determines $\kappa_2(a_0\sigma+b_0)$, and hence κ_2, and the absolute term in the coefficient of λ^4 similarly determines κ_4.

The excepted case in which κ contains odd as well as even powers of λ we may leave aside at present.

§ 3. We may apply the preceding to the much discussed* equation

$$\frac{d^2x}{d\theta^2}+(\sigma^2+2\lambda k_1\cos\theta+2\lambda^2k_2\cos 2\theta+\ldots)x = 0.$$

When $\lambda = 0$ we have the two factors $e^{i\sigma t}$, $e^{-i\sigma t}$, and the general case is that in which $e^{2i\sigma t}$ has not the period, 2π, of the coefficients in the differential equation, that is, when 2σ is not an integer. First assume this to be so. Then writing

$$x = e^{i\kappa\theta}X$$

we obtain

$$X''+2i\kappa X'+(\sigma^2-\kappa^2+2\lambda k_1\cos\theta+2\lambda^2k_2\cos 2\theta+\ldots)X = 0.$$

Herein assume

$$\kappa = \sigma+\kappa_2\lambda^2+\kappa_4\lambda^4+\ldots, \qquad X = 1+\lambda\phi_1+\lambda^2\phi_2+\ldots,$$

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* For this differential equation the following list of references may be useful, though it is probably far from complete:—MATHIEU, 'Louville's J.,' XIII. (1868), p. 137; HILL, 'Coll. Math. Works,' I., p. 255 ('Acta Math.,' VIII. (1886)); ADAMS, 'Coll. Scientific Papers,' I., p. 186, II., pp. 65, 86; TISSERAND, 'Méc. Cél.,' t. III., Ch. I.; POINCARÉ, 'Méth. Nouv.,' t. II., Ch. XVII.; FORSYTH, 'Linear Differential Equations' (1902), p. 431; RAYLEIGH, 'Scientific Papers,' vol. III. (1902), p. 1; LINDEMANN, 'Math. Annal.,' Bd. XXII. (1883), p. 117; LINDSTEDT, 'Astr. Nachr.,' 2503 (1883); LINDSTEDT, 'Mémoires de l'Acad. de St. Petersbourg,' t. XXI., No. 4; BRUNS, 'Astr. Nachr.,' 2533, 2553 (1883); CALLANDREAU, 'Astr. Nachr.,' 2547 (1883); CALLANDREAU, 'Ann. Observ.,' Paris, XXII. (1896); TISSERAND, 'Bull. Astr.,' t. IX. (1892); STIELTJES, 'Astr. Nachr.,' 2602, 2609 (1884); HARZER, 'Astr. Nachr.,' 2850, 2851 (1888); MOULTON and MACMILLAN, 'Amer. J.,' XXXIII. (1911); MOULTON, 'Rendic. Palermo,' XXXII. (1911); MOULTON, 'Math. Ann.,' LXXIII. (1913); WHITTAKER, 'Cambridge Congress' (1912), I., p. 366; WHITTAKER, YOUNG and MILNE, 'Edinburgh Math. Soc.,' XXXII., 1913–14; INCE, 'Monthly Not.,' Roy. Astr. Soc., LXXV. (1915); POINCARÉ, 'Bull. Astr.,' XVII. (1900).

where ϕ_r is an integral polynomial of order r in ζ and ζ^{-1}, the quantity $e^{i\theta}$ being denoted by ζ. Then we have

$$\Sigma\lambda^n\phi''_n+2i\,(\sigma+\kappa_2\lambda^2+\ldots)\,\Sigma\lambda^n\phi'_n$$
$$+\left[-2\sigma\kappa_2\lambda^2-(2\sigma\kappa_4+\kappa_2^2)\,\lambda^4+\ldots+2\lambda k_1\cos\theta+\ldots\right]\left[1+\Sigma\lambda^n\phi_n\right]=0.$$

The terms in λ give

$$\phi''_1+2i\sigma\phi'_1+k_1\,(\zeta+\zeta^{-1})=0,$$

which, if we denote $(\sigma+r)^2-\sigma^2$ or $r\,(2\sigma+r)$ by u_r, so that the result of substituting ζ^r for ϕ in $\phi''+2i\sigma\phi'$ is $-u_r\zeta^r$, leads to

$$\phi_1=k_1\left(\frac{\zeta}{u_1}+\frac{\zeta^{-1}}{u_{-1}}\right).$$

The terms in λ^2 give

$$\phi''_2+2i\sigma\phi'_2+k_1\,(\zeta+\zeta^{-1})\,\phi_1+k_2\,(\zeta^2+\zeta^{-2})-2\sigma\kappa_2=0,$$

which, if we write

$$\phi_2=A_2\zeta^2+A_{-2}\zeta^{-2},$$

leads to

$$A_2=\frac{1}{u_2}\left(k_2+\frac{k_1^2}{u_1}\right),\qquad A_{-2}=\frac{1}{u_{-2}}\left(k_2+\frac{k_1^2}{u_{-1}}\right)$$

and

$$\kappa_2=\frac{k_1^2}{2\sigma}\left(\frac{1}{u_1}+\frac{1}{u_{-1}}\right)=-\frac{k_1^2}{\sigma\,(4\sigma^2-1)}\,.$$

By the terms in λ^3, λ^4, we similarly find the coefficients in

$$\phi_3=A_3\zeta^3+A_{-3}\zeta^{-3}+B_1\zeta+B_{-1}\zeta^{-1},$$

$$\phi_4=A_4\zeta^4+A_{-4}\zeta^{-4}+B_2\zeta^2+B_{-2}\zeta^{-2},$$

and also

$$\kappa_4=-\frac{60\sigma^4-35\sigma^2+2}{4\sigma^3\,(\sigma^2-1)\,(4\sigma^2-1)^3}\,k_1^4+\frac{3}{2\sigma\,(\sigma^2-1)\,(4\sigma^2-1)}\,k_1^2k_2-\frac{1}{4\sigma\,(\sigma^2-1)}\,k_2^2.$$

If we change the notation, writing $\theta=2t$, $2\sigma=n$, so that the differential equation becomes

$$\frac{d^2x}{dt^2}+\left[n^2+8\lambda k_1\cos 2t+8\lambda^2k_2\cos 4t+\ldots\right]x=0$$

and

$$\zeta=e^{2it},\quad x=e^{2i\kappa t}X,$$

we have

$$\kappa=\tfrac{1}{2}n-\frac{2k_1^2\lambda^2}{n\,(n^2-1)}+\lambda^4\left\{-2\,\frac{15n^4-35n^2+8}{n^3\,(n^2-4)\,(n^2-1)^3}\,k_1^4+\frac{12k_1^2k_2}{n\,(n^2-4)\,(n^2-1)}-\frac{2k_2^2}{n\,(n^2-4)}\right\}+\ldots$$

It is clear that κ is essentially real so long as this series converges.

As an immediate application take the equation in BROWN'S 'Lunar Theory,' p. 107,

$$\frac{d^2x}{dt^2}+n^2x\left\{1+\tfrac{3}{2}m^2-\tfrac{9}{32}m^4+\left(3m^2+\tfrac{19}{2}m^3+\tfrac{137}{6}m^4\right)\cos 2\xi+\tfrac{33}{8}m^4\cos 4\xi\right\} = 0,$$

where

$$\xi = (n-n')\,t+\epsilon-\epsilon', \quad m = n'/n.$$

Put

$$m_1 = \frac{m}{1-m} = \frac{n'}{n-n'}, \quad m = \frac{m_1}{1+m_1}, \quad n\,dt = (1+m_1)\,d\xi\,;$$

then the equation becomes

$$\frac{d^2x}{d\xi^2}+x\left\{1+2m_1+\tfrac{5}{2}m_1^2-\tfrac{9}{32}m_1^4+m_1^2\left(3+\tfrac{19}{2}m_1+\tfrac{40}{3}m_1^2\right)\cos 2\xi+\tfrac{33}{8}m_1^4\cos 4\xi\right\} = 0,$$

which is of the form above, ξ replacing t. We may then take

$$\lambda = \frac{m_1^2}{8}, \quad n^2 = 1+2m_1+\tfrac{5}{2}m_1^2-\tfrac{9}{32}m_1^4, \quad k_1 = 3+\tfrac{19}{2}m_1+\tfrac{40}{3}m_1^2, \quad k_2 = 33.$$

Here m_1 is a small quantity and

$$\frac{\lambda^2}{n^2-1} = \frac{m_1^4}{64\,(2m_1+\ldots)} = \frac{m_1^3}{128}(1+\ldots)$$

is of the order m_1^3, while similarly $\lambda^4/(n^2-1)^3$ is of the order m_1^5. Also

$$\begin{aligned} n &= (1+m_1)\left\{1+\tfrac{3}{2}m_1^2\left(1-2m_1+3m_1^2\right)-\tfrac{9}{32}m_1^4\right\}^{\frac{1}{2}} \\ &= (1+m_1)\left(1+\tfrac{3}{4}m_1^2-\tfrac{3}{2}m_1^3+\tfrac{117}{64}m_1^4\right). \end{aligned}$$

Thus

$$\begin{aligned} \kappa &= \tfrac{1}{2}n\left\{1-\frac{4k_1^2\lambda^2}{n^2\,(n^2-1)}\right\} \\ &= \tfrac{1}{2}\,(1+m_1)\left(1+\tfrac{3}{4}m_1^2-\tfrac{57}{32}m_1^3+\tfrac{123}{128}m_1^4\right), \end{aligned}$$

which is easily seen to agree with the result given by BROWN, or by ADAMS, 'Coll. Works,' I., p. 187, when we take account of the fact that

$$2i\kappa\xi = 2i\kappa\,(n-n')\,t = 2i\kappa\,\frac{n-n'}{n}\,nt,$$

so that, in terms of the quantity denoted by g,

$$\kappa = \tfrac{1}{2}\,(1+m_1)\,g.$$

This example is chiefly useful here as calling attention to the fact that n^2, while not exactly equal to 1, is near to it, and consequently the factor $\lambda/(n^2-1)$ is only small of the first order in m_1. The same weakness occurs in the terms in ζ^{-1}, ..., in the solution.

§ 4. In the equation considered by HILL (' Coll. Works,' I., p. 268) the ratio $4k_1\lambda/(n^2-1)$ is about $(2{\cdot}785)^{-1}$, and there is a term slightly greater than $4k_1\lambda\,(2{\cdot}785)^{-r}$ arising in the terms in λ^{r+1} in the series for κ, in which $4k_1\lambda$ is about $0{\cdot}5704$; and the series fails absolutely in cases in which n is an integer. Then the assumption that κ is a power series in λ^2, and the terms in X which are independent of λ, must be modified, for reasons above given. The series when n is an integer has been considered by TISSERAND, ' Bull. Astr.,' IX., 1892; modifying his procedure, so as to include the case when n is near to 1 as well as that in which $n = 1$, we may write, in accordance with the suggestion of such examples as that above quoted,

$$n^2 = 1+4\lambda h_1+4\lambda^2 h_2+\ldots,$$

and then, denoting $e^{2irt}+e^{-2irt}$ by w_r, consider the equation

$$\frac{d^2x}{dt^2}+[1+4\lambda\,(h_1+k_1w_1)+4\lambda^2\,(h_2+k_2w_2)+\ldots]\,x = 0.$$

By the changes

$$\tau = 2it, \quad \zeta = e^\tau,$$

$$-ix = e^{-i(1+2q)t}\,[\mathrm{U}-\mathrm{V}\zeta], \quad \frac{dx}{dt} = e^{-i(1+2q)t}\,[\mathrm{U}+\mathrm{V}\zeta],$$

the differential equation may be replaced by the pair

$$\frac{d\mathrm{U}}{d\tau}-q\mathrm{U} = -\phi\,(\mathrm{U}-\mathrm{V}\zeta), \quad \frac{d\mathrm{V}}{d\tau}-q\mathrm{V} = -\phi\,(\mathrm{U}\zeta^{-1}-\mathrm{V}),$$

where

$$w_r = \zeta^r+\zeta^{-r},$$

$$\phi = \lambda\,(h_1+k_1w_1)+\lambda^2\,(h_2+k_2w_2)+\ldots.$$

Assuming here

$$q = \lambda q_1+\lambda^2 q_2+\ldots,$$

$$\mathrm{U} = 1+\lambda u_1+\lambda^2 u_2+\ldots, \quad \mathrm{V} = \mathrm{B}\,(1+\lambda v_1+\lambda^2 v_2+\ldots),$$

in which B is a constant, and u_r, v_s are polynomials in ζ and ζ^{-1}, we find, equating coefficients of like powers of λ,

$$-\frac{du_r}{d\tau}+q_1u_{r-1}+q_2u_{r-2}+\ldots+q_r = \mathrm{H}_r,$$

$$-\frac{dv_r}{d\tau}+q_1v_{r-1}+q_2v_{r-2}+\ldots+q_r = \mathrm{K}_r,$$

in which

$$\mathrm{H}_r = (h_1+k_1w_1)\,(u_{r-1}-\zeta\mathrm{B}v_{r-1})+(h_2+k_2w_2)\,(u_{r-2}-\zeta\mathrm{B}v_{r-2})+\ldots+(h_r+k_rw_r)\,(1-\zeta\mathrm{B}),$$

$$\mathrm{K}_r = \zeta^{-1}\mathrm{B}^{-1}\mathrm{H}_r.$$

In these equations, as u_r, v_s are to be polynomials in ζ, ζ^{-1}, the absolute terms, those involving ζ^0, must vanish. For $r = 1$ this gives

$$h_1 - q_1 = k_1\mathrm{B}, \quad h_1 + q_1 = k_1\mathrm{B}^{-1}.$$

We thus write, using hyperbolic functions,

$$h_1 = k_1 ch\alpha, \qquad q_1 = k_1 sh\alpha, \qquad \mathrm{B} = e^{-\alpha}.$$

With these we find at once by integration the values of u_1, v_1, save for the absolute terms in these, which we denote by P_1, Q_1 respectively. The conditions for these are to be found by considering the absolute terms in the equations for $r = 2$; and so on continually. In general, when we have found

$$u_1, v_1, u_2, v_2, \ldots, u_{r-1}, v_{r-1},$$

and have found u_r, v_r, save for their absolute terms, P_r, Q_r, we find, on taking the absolute terms in the equations which involve $du_{r+1}/d\tau$ and $dv_{r+1}/d\tau$, and adding and subtracting these terms, that the two quantities

$$k_1 sh\alpha\,(\mathrm{P}_r - \mathrm{Q}_r) - h_{r+1}, \qquad k_1 ch\alpha\,(\mathrm{P}_r - \mathrm{Q}_r) - q_{r+1}$$

are thereby expressed in terms of known quantities. It is at once seen that there would be no loss of generality in putting P_1, P_2, P_3, ... all zero. Carrying out the work, and writing M_r for $\mathrm{P}_r - \mathrm{Q}_r$, we obtain

$$q = k_1 sh\alpha\lambda + (\mathrm{M}_1 k_1 ch\alpha - k_1^2 sh2\alpha)\,\lambda^2$$
$$+ \{\tfrac{1}{2}\mathrm{M}_1^2 k_1 c^{\alpha} - 2\mathrm{M}_1 k_1^2 ch2\alpha + k_1^3 sh\alpha\,(6ch^2\alpha - \tfrac{11}{4}) + k_1 k_2 sh\alpha + k_1 ch\alpha\,(\mathrm{M}_2 - \mathrm{M}_1\mathrm{P}_1)\}\,\lambda^3 + \ldots,$$

where

$$h_1 = k_1 ch\alpha,$$

$$h_2 = \mathrm{M}_1 k_1 sh\alpha - \tfrac{1}{2}k_1^2 ch2\alpha,$$

$$h_3 = \tfrac{1}{2}\mathrm{M}_1^2 k_1 c^{\alpha} - \mathrm{M}_1 k_1^2 sh2\alpha + k_1^3 ch\alpha\,(2sh^2\alpha - \tfrac{1}{4}) + k_1 k_2 ch\alpha + k_1 sh\alpha\,(\mathrm{M}_2 - \mathrm{M}_1\mathrm{P}_1).$$

Also

$$-ixe^{i(1+2q)t} = 1 - c^{-\alpha}\zeta + \lambda\mathrm{W}_1 + \lambda^2\mathrm{W}_2 + \ldots$$

in which

$$\mathrm{W}_1 = \tfrac{1}{2}k_1\zeta^{-1} + \mathrm{P}_1 - k_1 sh\alpha + (-\mathrm{P}_1 + \mathrm{M}_1 - k_1 sh\alpha)\,e^{-\alpha}\zeta - \tfrac{1}{2}k_1 e^{-\alpha}\zeta^2,$$

$$\mathrm{W}_2 = \tfrac{1}{6}\zeta^{-2}(k_2 + \tfrac{1}{2}k_1^2) + \zeta^{-1}[\tfrac{1}{2}\mathrm{P}_1 k_1 - \tfrac{1}{2}k_2 e^{-\alpha} + k_1^2(\tfrac{1}{4}e^{-\alpha} - sh\alpha)]$$
$$+ \mathrm{P}_2 - \mathrm{P}_1 k_1 sh\alpha - \mathrm{M}_1 k_1 ch\alpha + k_1^2 sh\alpha\,(ch\alpha + e^{\alpha})$$
$$- \zeta e^{-\alpha}[\mathrm{P}_2 - \mathrm{M}_2 + \mathrm{P}_1 k_1 sh\alpha + \mathrm{M}_1 k_1 e^{-\alpha} - k_1^2 sh\alpha\,(ch\alpha + e^{-\alpha})]$$
$$+ \zeta^2 e^{-\alpha}[-\tfrac{1}{2}\mathrm{P}_1 k_1 + \tfrac{1}{2}\mathrm{M}_1 k_1 + \tfrac{1}{2}k_2 e^{\alpha} - k_1^2(sh\alpha + \tfrac{1}{4}e^{\alpha})]$$
$$- \tfrac{1}{6}\zeta^3 e^{-\alpha}(k_2 + \tfrac{1}{2}k_1^2).$$

If from these formulæ we determine M_1 and $M_2-M_1P_1$ in terms of h_2 and h_3 we find for q,

$$q = k_1 sh\alpha\lambda + H_2 cth\alpha \,.\, \lambda^2$$
$$+\lambda^3\left[-\frac{H_2^{\,2}}{2k_1 sh^3\alpha} - \frac{2k_1H_2ch^2\alpha}{sh\alpha} + \frac{h_3ch\alpha - k_1k_2 - \frac{1}{4}k_1^{\,3}(2sh^2\alpha-1)}{sh\alpha}\right] + \ldots,$$

where

$$H_2 = h_2 - \tfrac{1}{2}k_1^{\,2}(2sh^2\alpha - 1).$$

This formulæ is apparently unsatisfactory when $sh\alpha$ is small, or n^2-1 nearly equal to $4\lambda k_1$. In fact, the series is of the form

$$a + \frac{b}{2a}\lambda + \frac{4ca^2-b^2}{8a^3}\lambda^2 + \frac{8a^4d-4a^2bc+b^3}{16a^5}\lambda^3 + \ldots,$$

whose square has a form in which we can put $a = 0$. On squaring, we have

$$q^2 = (h_1^{\,2}-k_1^{\,2})\lambda^2 + 2h_1H_2\lambda^3 + \lambda^4(H_2^{\,2} - 4h_1^{\,2}H_2 + 2h_1h_3 - 2k_1^{\,2}k_2 - h_1^{\,2}k_1^{\,2} + \tfrac{3}{2}k_1^{\,4}) + \ldots,$$

wherein

$$H_2 = h_2 - h_1^{\,2} + \tfrac{3}{2}k_1^{\,2},$$

and this form is appropriate when $\alpha = 0$ or $h_1 = k_1$. In particular, when $h_2 = h_3 = \ldots = 0$, but h_1 is not zero, this gives

$$q^2 = (h_1^{\,2}-k_1^{\,2})\lambda^2 + h_1(3k_1^{\,2}-2h_1^{\,2})\lambda^3 + [5(h_1^{\,2}-k_1^{\,2})^2 - \tfrac{5}{4}k_1^{\,4} - 2k_1^{\,2}k_2]\lambda^4 + \ldots,$$

a formula reproducing the former if $h_1+h_2\lambda+h_3\lambda^2$ be put for h_1. It will be seen in Part II. of this paper why the form of q^2 is comparatively so simple.

Brief reference may be made to another way in which we may use the foregoing equations, regarding h_1, h_2, h_3, ... not as given constants but as quantities to be determined to simplify the result; this has been adopted by Prof. WHITTAKER (' Proc. Math. Soc.,' Edinburgh, XXXII., 1913–14) who chooses as his condition that no terms in ζ°, ζ^1 shall occur in W_1, W_2, ..., in the expression for x. This can be secured by taking

$$P_1 = k_1 sh\alpha, \quad M_1 = 2k_1 sh\alpha, \quad P_2 = 0, \quad Q_2 = 0, \ \ldots.$$

From our present point of view a more natural procedure is to take $P_1 = 0 = Q_1 = P_2 = Q_2 = \ldots.$ Then we obtain

$$n^2 = 1 + \lambda k_1 ch\beta - \tfrac{1}{2}\lambda^2k_1^{\,2}ch2\beta + \lambda^3[k_1^{\,3}ch\beta(2sh^2\beta - \tfrac{1}{4}) + k_1k_2ch\beta] + \ldots,$$

where we have written β in place of α, as this argument is now supposed to be determined, from this equation, corresponding to a given value of n^2. When β is so determined, q is given by

$$q = k_1\lambda sh\beta - k_1^{\,2}\lambda^2 sh2\beta + \lambda^3[k_1^{\,3}sh\beta(6ch^2\beta - \tfrac{11}{4}) + k_1k_2sh\beta] + \ldots,$$

an equation which does not contain $sh\beta$ in its denominator. With a view to the comparison of this method with the two others given in the present paper we consider two examples. First, for the equation

$$\frac{d^2x}{dt^2}+[1+4\lambda k_1w_1+4\lambda^2k_2w_2+\ldots]\,x = 0,$$

for which n^2 is actually unity, we should determine β so that

$$0 = k_1ch\beta-\tfrac{1}{2}k_1{}^2ch2\beta+k_1{}^3ch\beta\,(2sh^2\beta-\tfrac{1}{4})+k_1k_2ch\beta+\ldots,$$

where we have replaced λ by 1. This gives approximately

$$ch\beta = -\tfrac{1}{2}k_1\,(1+\tfrac{7}{4}k_1{}^2-k_2), \quad sh\beta = i\,(1-\tfrac{1}{8}k_1{}^2),$$

and hence

$$q = ik_1\,(1-\tfrac{15}{8}k_1{}^2+k_2+\ldots),$$

while the value for β, substituted for α, gives the series for x. We may remark that for the equation

$$\frac{d^2x}{dt^2}+(1+8k_1\cos 2t)\,x = 0,$$

TISSERAND ('Bull. Astr.,' IX., 1892, p. 102) finds

$$q = ik_1\left(1-\tfrac{15}{8}k_1{}^2+\frac{9719}{2^7\,.\,3^2}\,k_1{}^4+\ldots\right).$$

As a further example take

$$\frac{d^2x}{dt^2}+x\,[1+4k_1\,(1+w_1)+4k^2w_2+\ldots] = 0,$$

which, as will appear, is an interesting equation. Then β is to be found from

$$k_1 = k_1ch\beta-\tfrac{1}{2}k_1{}^2ch2\beta+k_1{}^3ch\beta\,(2sh^2\beta-\tfrac{1}{4})+k_1k_2ch\beta+\ldots,$$

so that

$$ch\beta = 1+\tfrac{1}{2}k_1+\tfrac{5}{4}k_1{}^2-k_2+\tfrac{7}{8}k_1{}^3-\tfrac{5}{2}k_1k_2+\ldots,$$

$$sh\beta = (k_1)^{\frac{1}{2}}\left(1+\tfrac{11}{8}k_1-\frac{k_2}{k_1}+\ldots\right),$$

and hence

$$q = (k_1)^{\frac{1}{2}}\,(k_1-\tfrac{5}{8}k_1{}^2-k_2+\ldots).$$

In both these examples the value found for q follows at once from the general formula above given for q^2, of which a further deduction is found below in Part II. In the last example the value found for β gives a solution for x in a series involving $(k_1)^{\frac{1}{2}}$. It will be seen in Part II. that when x involves $(k_1)^{\frac{1}{2}}$, it is in a very simple way, and the case seems better treated as there explained. The occurrence of $(k_1)^{\frac{1}{2}}$ in the value of q, in certain cases, is a particular case of POINCARÉ'S theorem, 'Méth. Nouv.,' I., § 79, p. 219. The phenomenon presents itself, however, as a consequence of the use of elliptic functions in TISSERAND'S theory of the small planets; see TISSERAND, 'Méc. Cél.,' IV., p. 426 (or 'Bull. Astr.,' IV.).

§ 5. A very important question in regard to the differential equation under discussion is whether q is real or not, since upon this depends the conventional stability of the secondary oscillation determined by the differential equation. We have remarked above (§ 3) that when n is not an integer, and $k_1\lambda$, $k_2\lambda^2$, ... are small enough to render the series there obtained convergent, the value of q is necessarily real. The cases in which n is an integer and $k_2 = 0 = k_3 = \ldots$ have been discussed by TISSERAND, 'Bull. Astr.,' IX., 1892, who obtains the result that the motion is unstable for $n = 1$ or $n = 2$, that is for the equations

$$\frac{d^2x}{dt^2} + [1+4\lambda k_1 w_1]\, x = 0, \quad \frac{d^2x}{dt^2} + [4+4\lambda k_1 w_1]\, x = 0,$$

when λ is small enough, but stable for greater integer values of n. The formula for q^2, given in the earlier part of § 4 preceding, shows that for cases in which

$$n^2 = 1+4h_1\lambda$$

the motion is stable provided

$$(h_1/k_1)^2 > 1,$$

the values of $ch\alpha$ and $sh\alpha$ being then both real. It shows further that it is stable for

$$h_1 = \pm k_1 = \text{positive}$$

provided λ be small enough. The critical equation is thus

$$\frac{d^2x}{dt^2} + x\,[1+4k_1(1+w_1)+4k_2 w_2+\ldots] = 0,$$

the other sign of k_1 being obtainable by changing t into $t+\frac{\pi}{2}$.

§ 6. We proceed now to the case when $n = 2$.

If in the equation

$$\frac{d^2x}{dt^2} + x\,[m^2+4\lambda\,(h_1+k_1 w_1)+4\lambda^2(h_2+k_2 w_2)+\ldots] = 0,$$

in which m is an integer, we put

$$\tau = 2it, \quad \zeta = e^{\tau},$$

$$\mathrm{U} = \tfrac{1}{2}e^{\frac{1}{2}m\tau+q\tau}\left(\frac{dx}{dt}-imx\right), \quad \mathrm{V} = \tfrac{1}{2}e^{-\frac{1}{2}m\tau+q\tau}\left(\frac{dx}{dt}+imx\right),$$

we obtain

$$\frac{dU}{d\tau}-qU = -\frac{\phi}{m}(U-V\zeta^{m}), \quad \frac{dV}{d\tau}-qV = -\frac{\phi}{m}(U\zeta^{-m}-V),$$

where

$$\phi = \lambda\,(h_1+k_1w_1)+\lambda^2\,(h_2+k_2w_2)+\ldots,$$

$$w_r = \zeta^{r}+\zeta^{-r}.$$

We may then further substitute

$$W = U\zeta^{-m}-V, \quad U_1 = mU,$$

leading to

$$\frac{dU_1}{d\tau}-qU_1 = -\phi\zeta^{m}W,$$

$$\frac{dW}{d\tau}-qW = -\zeta^{-m}U_1,$$

where

$$x = \frac{i}{m}\,e^{\frac{1}{2}m\tau-q\tau}W.$$

These equations can be solved by writing

$$q = \lambda q_1+\lambda^2 q_2+\ldots,$$

$$U_1 = 1+\lambda u_1+\lambda^2 u_2+\ldots, \quad W = \frac{A+\zeta^{-m}}{m}+\lambda w_1+\lambda^2 w_2+\ldots,$$

where A is a constant, and $u_1, u_2, \ldots, w_1, w_2, \ldots$ are polynomials in ζ, ζ^{-1}.

For $m = 2$, in particular, we find that if $h_1 = 0$, the quantity A is required, and determined in the course of the work, and $q_1 = 0$. But if h_1 is not zero, we must take $A = 0$, and obtain $q_1 = \frac{1}{2}h_1$, the succeeding $q_2, q_3, \ldots$ being real. In fact, as far as λ^3,

$$q = \tfrac{1}{2}h_1\lambda-(\tfrac{1}{8}h_1^2+\tfrac{1}{3}k_1^2-\tfrac{1}{2}h_2)\,\lambda^2+\left\{\frac{h_1^3}{16}+\tfrac{11}{18}h_1k_1^2-\frac{h_1h_2}{4}+\frac{h_3}{2}-\frac{(k_1^2-k_2)^2}{4h_1}\right\}\lambda^3+\ldots,$$

which gives

$$q^2 = \tfrac{1}{4}h_1^2\lambda^2-h_1\,(\tfrac{1}{8}h_1^2+\tfrac{1}{3}k_1^2-\tfrac{1}{2}h_2)\,\lambda^3$$
$$+\left\{\tfrac{5}{64}h_1^4+\tfrac{25}{36}h_1^2k_1^2-\tfrac{5}{36}k_1^4+\tfrac{1}{2}k_1^2k_2-\tfrac{1}{4}k_2^2-h_2\,(\tfrac{3}{8}h_1^2+\tfrac{1}{3}k_1^2)+\tfrac{1}{4}h_2^2+\tfrac{1}{2}h_1h_3\right\}\lambda^4+\ldots.$$

We know, as is shown in Part II. of this paper, that the form of q^2 is valid even when $h_1 = 0$. Then we have

$$q^2 = \tfrac{1}{4}\lambda^4\,(h_2+k_2-\tfrac{5}{3}k_1^2)\,(h_2-k_2+\tfrac{1}{3}k_1^2)+\ldots,$$

which, when $h_2 = 0$, is only positive, provided

$$5k_1^2 > 3k_2 > k_1^2.$$

The case discussed by Tisserand is that in which $k_2 = k_3 = \ldots = 0$. Then

$$q = \frac{k_1{}^2\lambda^2}{6}\sqrt{(-5)},$$

and the quantity A in the formula for W, or x, is found to be $\frac{1}{3}(-2 \pm \sqrt{-5})$.

When $m = 3$, for the equation

$$\frac{d^2x}{dt^2} + (9 + 8\lambda k \cos 2t)\, x = 0,$$

we find $A = 0$, and

$$q = -\frac{k^2\lambda^2}{12} - \frac{269}{64\,.\,27\,.\,5}k^4\lambda^4 + \ldots,$$

$$U_1 = 1 - \tfrac{1}{3}\lambda k(\zeta - \zeta^{-1}) + \ldots, \quad W = \tfrac{1}{3}\zeta^{-3} + \tfrac{1}{3}\lambda k(\tfrac{1}{4}\zeta^{-4} - \tfrac{1}{2}\zeta^{-2} + \tfrac{1}{5}) + \ldots.$$

The question of the reality of q, in cases where $k_2 = 0 = k_3 = \ldots$, is discussed by Poincaré, 'Méth. Nouv.,' II. (1893), p. 243, and by Callandreau, 'Ann. Observ.,' Paris, XXII. (1896), p. 23. So far the results are :—

(1) For the equation at the bottom of p. 135 (§ 3) q is real when n^2 is not an integer, provided the series obtained converges.

(2) This condition does not however include, for instance, the case when n^2 is near to unity. For q is imaginary, for the equation

$$\frac{d^2x}{dt^2} + [n^2 + 8k_1 \cos 2t + \ldots]\, x = 0,$$

if $(n^2-1)^2 < (4k_1)^2$. It is real if $(n^2-1)^2 > (4k_1)^2$, and real if n^2-1 is positive and equal to $\pm 4k_1$. This has been proved here.

(3) q may be real when n is just greater than 2, when $k_1, k_2, \ldots$ are small enough. This has been proved here.

(4) q is real when n is any integer greater than 2, if $k_2 = k_3 = \ldots = 0$, but imaginary when $n = 1$ or $n = 2$. This result is given by Tisserand and Callandreau, as above.*

[*October 30, 1915*.—It may be worth adding, in connexion with the numerical results given in § 6, that the equation

$$\frac{d^2x}{dt^2} + c \sin t\,.\,x = 0,$$

in which c is small, is solved by

$$x = e^{i\lambda t}U,$$

---

* See the note at the conclusion of § 21 (p. 184).

in which, as far as c^3,

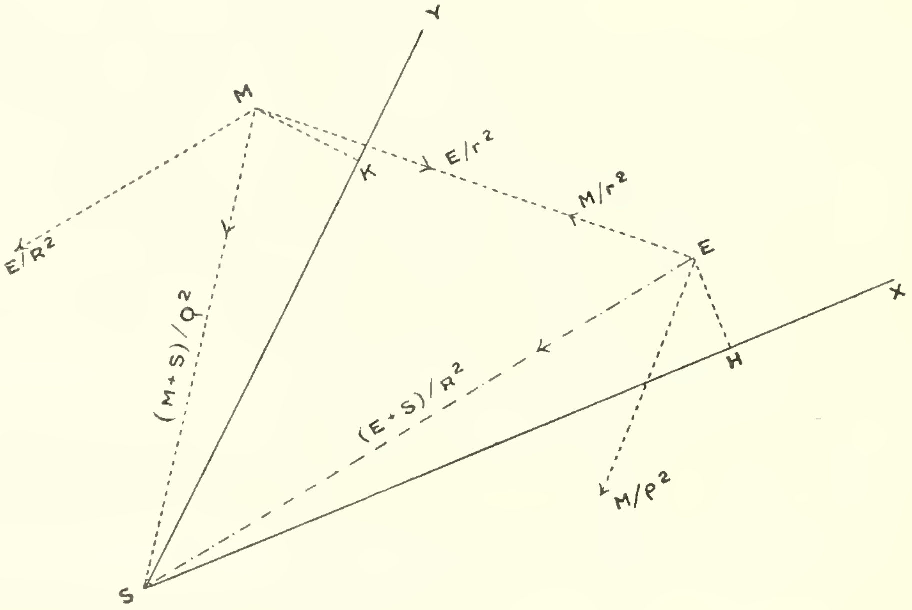
$$\lambda = \frac{c}{\sqrt{2}}\left(1+\tfrac{25}{32}c^2\right),$$

and, as far as c^4,

$$\mathrm{U} = 1+c\sin t+c^2\left(i\sqrt{2}\cos t-\tfrac{1}{8}\cos 2t\right)+c^3\left(\tfrac{25}{16}\sin t+\frac{3i}{8\sqrt{2}}\sin 2t-\frac{\sin 3t}{144}\right)$$
$$+c^4\left(\frac{31}{8\sqrt{2}}i\cos t-\tfrac{53}{144}\cos 2t-\frac{11}{432\sqrt{2}}i\cos 3t+\frac{\cos 4t}{4608}\right).\,\Big]$$

§ 7. We pass now to the consideration of a pair of simultaneous differential equations arising in the consideration of the stability of the motion of three particles occupying the angular points of an equilateral triangle moving under their mutual gravitation.

The stability of this motion has been discussed by ROUTH ('Proc. Lond. Math. Soc.,' VI., 1875; 'Rigid Dynamics,' II., p. 61) in the case when the relative paths of the particles are circles.* In what follows we do not assume this.



The three particles being S, E, M, take an axis through S, say SX, rotating with angular velocity $\dot{\theta}$, the line SE being supposed to coincide very nearly with SX. Draw a perpendicular EH from E to SX, denote EH by y, and SH by $\mathrm{A}+x$, where x, y will be considered small, their squares being neglected, but A is a variable finite quantity. Draw a second axes SY through S at a constant angle $\frac{\pi}{3}$ with SX, and

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* The following references may be of use:—CHARLIER, 'Die Mechanik des Himmels,' and 'Astr. Nachr.,' 193, 15; STOCKWELL, 'Astron. Journ.,' 557 (1904); LINDERS, 'Arkiv for Mat.' (Stockholm), IV., No. 20; BROWN, 'Monthly Notices, R.A.S.,' LXXI. (1911), pp. 439, 492; HEINRICH, 'Astr. Nachr.,' 194, 12 (December, 1912); BLOCK, 'Arkiv for Mat.,' X., 4 (1914).

similarly, draw a perpendicular MK from M to SY; denote SK, KM by $A+\xi$ and η. If $R = SE$, $r = EM$, $\rho = MS$, we have, with proper conventions of sign,

$$R^2 = (A+x)^2+y^2, \qquad \rho^2 = (A+\xi)^2+\eta^2,$$

$$r^2 = [\tfrac{1}{2}(A+\xi)-\tfrac{1}{2}\eta\sqrt{3}-A-x]^2+[\tfrac{1}{2}(A+\xi)\sqrt{3}+\tfrac{1}{2}\eta-y]^2.$$

The accelerations of E, relatively to S, parallel to SX and parallel to HE, are, respectively,

$$-(E+S)\frac{A+x}{R^3}+M\frac{\frac{1}{2}(A+\xi)-\frac{1}{2}\eta\sqrt{3}-(A+x)}{r^3}-M\frac{\frac{1}{2}(A+\xi)-\frac{1}{2}\eta\sqrt{3}}{\rho^3},$$

$$-(E+S)\frac{y}{R^3}+M\frac{\frac{1}{2}(A+\xi)\sqrt{3}+\frac{1}{2}\eta-y}{r^3}-M\frac{\frac{1}{2}\eta+\frac{1}{2}(A+\xi)\sqrt{3}}{\rho^3};$$

the accelerations of M, relatively to S, parallel to SY and parallel to KM, are, respectively,

$$-(M+S)\frac{A+\xi}{\rho^3}-E\left(\frac{1}{2}\cdot\frac{\frac{1}{2}(A+\xi)-\frac{1}{2}\eta\sqrt{3}-(A+x)}{r^3}+\frac{\sqrt{3}}{2}\cdot\frac{\frac{1}{2}(A+\xi)\sqrt{3}+\frac{1}{2}\eta-y}{r^3}\right)$$
$$-E\frac{\frac{1}{2}(A+x)+\frac{1}{2}y\sqrt{3}}{R^3},$$

$$-(M+S)\frac{\eta}{\rho^3}-E\left(\frac{1}{2}\cdot\frac{\frac{1}{2}(A+\xi)+\frac{1}{2}\eta-y}{r^3}-\frac{\sqrt{3}}{2}\cdot\frac{\frac{1}{2}(A+\xi)-\frac{1}{2}\eta\sqrt{3}-A-x}{r^3}\right)$$
$$-E\cdot\frac{\frac{1}{2}y-\frac{1}{2}(A+x)\sqrt{3}}{R^3}.$$

If, then, in the equations of motion relatively to S, after expanding in powers of x, y, ξ, η, we equate the finite and the small parts, the squares of x, y, ξ, η being neglected, we obtain

$$\ddot{A}-A\dot{\theta}^2 = -\frac{\mu}{A^2}$$

and

$$A^2\dot{\theta} = \text{constant}, = h, \text{ say},$$

where

$$\mu = S+E+M, \quad \dot{\theta} = \frac{d\theta}{dt}, \quad \ddot{\theta} = \frac{d^2\theta}{dt^2}, \text{ \&c.},$$

together with

$$\ddot{X}-2\dot{\theta}\dot{Y}-\ddot{\theta}Y-\left(\dot{\theta}^2-\frac{\mu}{A^3}\right)X = \frac{3\sqrt{3}}{4A^3}\left[\frac{4S+E+M}{\sqrt{3}}X+(E-M)Y\right],$$

$$\ddot{Y}+2\dot{\theta}\dot{X}+\ddot{\theta}X-\left(\dot{\theta}^2-\frac{\mu}{A^3}\right)Y = \frac{3\sqrt{3}}{4A^3}[(E-M)X+\sqrt{3}(E+M)Y],$$

in which X, Y respectively denote $\xi - x$ and $\eta - y$, and also

$$\ddot{x} - 2\dot{\theta}\dot{y} - \ddot{\theta}y - \left(\dot{\theta}^2 - \frac{\mu}{\text{A}^3}\right)x = \frac{3\sqrt{3}\text{M}}{4\text{A}^3}\left[\frac{4\mu}{\text{M}\sqrt{3}}x + \text{X}\sqrt{3} + \text{Y}\right],$$

$$\ddot{y} + 2\dot{\theta}\dot{x} + \ddot{\theta}x - \left(\dot{\theta}^2 - \frac{\mu}{\text{A}^3}\right)y = \frac{3\sqrt{3}\text{M}}{4\text{A}^3}[\text{X} - \text{Y}\sqrt{3}].$$

The first equations have integrals expressible by

$$\frac{l}{\text{A}} = 1 + 2\lambda\cos\theta, \qquad \frac{h^2}{l} = \mu,$$

the point (A, θ) moving in an ellipse of eccentricity 2λ and semilatusrectum l. With these values the other equations are much simplified if we take θ, instead of the time t, as independent variable, as was pointed out to me by Mr. H. M. GARNER, of St. John's College, Cambridge. With this change they become

$$\left.\begin{aligned}(1+2\lambda\cos\theta)(\text{X}''-2\text{Y}'-\text{X}) - 4\lambda\sin\theta(\text{X}'-\text{Y}) &= a\text{X}+h\text{Y},\\ (1+2\lambda\cos\theta)(\text{Y}''+2\text{X}'-\text{Y}) - 4\lambda\sin\theta(\text{Y}'+\text{X}) &= h\text{X}+b\text{Y},\end{aligned}\right\} \quad . \quad . \quad (\text{I.})$$

where

$$a = \frac{8\text{S}-\text{E}-\text{M}}{4\mu}, \qquad h = \frac{3(\text{E}-\text{M})\sqrt{3}}{4\mu}, \qquad b = \frac{-4\text{S}+5(\text{E}+\text{M})}{4\mu},$$

and

$$\text{X}' = \frac{d\text{X}}{d\theta}, \qquad \text{X}'' = \frac{d^2\text{X}}{d\theta^2}, \text{ \&c.,}$$

together with

$$\left.\begin{aligned}(1+2\lambda\cos\theta)(x''-2y'-x) - 4\lambda\sin\theta(x'-y) - 2x &= \frac{3\sqrt{3}\text{M}}{4\mu}(\text{X}\sqrt{3}+\text{Y}),\\ (1+2\lambda\cos\theta)(y''+2x'-y) - 4\lambda\sin\theta(y'+x) + y &= \frac{3\sqrt{3}\text{M}}{4\mu}(\text{X}-\text{Y}\sqrt{3}).\end{aligned}\right\} \quad . \quad (\text{II.})$$

The first thing then is to solve the equations (I.), after which the right side in (II.) will be known. Considerable simplification can be introduced by change of notation; let $w = \exp\left(\frac{2\pi i}{3}\right)$, $w^2 = \exp\left(\frac{4\pi i}{3}\right)$,

$$\text{A} = \tfrac{1}{2}(a+b+2) = \tfrac{3}{2}, \quad \text{H} = \tfrac{1}{2}(a-b+2ih), \quad \text{K} = \tfrac{1}{2}(a-b-2ih),$$

so that

$$\text{H} = \tfrac{3}{2}\,\frac{\text{S}+w\text{E}+w^2\text{M}}{\text{S}+\text{E}+\text{M}}, \quad \text{K} = \tfrac{3}{2}\,\frac{\text{S}+w^2\text{E}+w\text{M}}{\text{S}+\text{E}+\text{M}}, \quad \text{HK} = \tfrac{9}{4}\left(1-\frac{m^2}{9}\right),$$

where

$$m^2 = 27\,\frac{\text{SE}+\text{SM}+\text{EM}}{(\text{S}+\text{E}+\text{M})^2};$$

further

$$p = \mathrm{A} + (\mathrm{HK})^{\frac{1}{2}} = \tfrac{3}{2}\left[1 + \left(1 - \frac{m^2}{9}\right)^{\frac{1}{2}}\right], \quad q = \mathrm{A} - (\mathrm{HK})^{\frac{1}{2}} = \tfrac{3}{2}\left[1 - \left(1 - \frac{m^2}{9}\right)^{\frac{1}{2}}\right],$$

so that

$$p+q = 3, \quad pq = \tfrac{1}{4}m^2.$$

Also

$$u = (1+2\lambda\cos\theta)(\mathrm{X}+i\mathrm{Y}), \quad v = (1+2\lambda\cos\theta)(\mathrm{X}-i\mathrm{Y}),$$

whereby the equations (I.) become

$$\left.\begin{aligned}(1+2\lambda\cos\theta)(u''+2iu') &= \mathrm{A}u+\mathrm{H}v,\\ (1+2\lambda\cos\theta)(v''-2iv') &= \mathrm{K}u+\mathrm{A}v,\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (\mathrm{I.})'$$

in which $u' = du/d\theta$, &c., and then

$$\Phi = \mathrm{K}^{\frac{1}{2}}u+\mathrm{H}^{\frac{1}{2}}v, \quad i\Psi = \mathrm{K}^{\frac{1}{2}}u-\mathrm{H}^{\frac{1}{2}}v,$$

so that Φ, Ψ are both real, and

$$\Phi+i\Psi = 2\mathrm{K}^{\frac{1}{2}}(1+2\lambda\cos\theta)(\mathrm{X}+i\mathrm{Y}), \quad \Phi-i\Psi = 2\mathrm{H}^{\frac{1}{2}}(1+2\lambda\cos\theta)(\mathrm{X}-i\mathrm{Y}),$$

and the equations (I.) become

$$\left.\begin{aligned}(1+2\lambda\cos\theta)(\Phi''-2\Psi') &= p\Phi,\\ (1+2\lambda\cos\theta)(\Psi''+2\Phi') &= q\Psi,\end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (\mathrm{I.})''$$

in which, beside the eccentricity 2λ, there are the two constants p, q, which are dependent upon the single number m.

The equations (II.), by means of the changes

$$\mathrm{U} = (1+2\lambda\cos\theta)(x+iy), \quad \mathrm{V} = (1+2\lambda\cos\theta)(x-iy),$$

become

$$\left.\begin{aligned}(1+2\lambda\cos\theta)(\mathrm{U}''+2i\mathrm{U}') - \tfrac{3}{2}(\mathrm{U}+\mathrm{V}) &= \frac{3\mathrm{M}}{2\mu}(1-w^2)\,v,\\ (1+2\lambda\cos\theta)(\mathrm{V}''-2i\mathrm{V}') - \tfrac{3}{2}(\mathrm{U}+\mathrm{V}) &= \frac{3\mathrm{M}}{2\mu}(1-w)\,u.\end{aligned}\right\} \quad . \; . \; . \quad (\mathrm{II.})'$$

Consider now the equations (I.)″. We know that the solutions are of the form

$$\Phi = \mathrm{C}e^{i\kappa\theta}\mathrm{F}+\mathrm{C}_1e^{i\kappa_1\theta}\mathrm{F}_1+\mathrm{C}_2e^{i\kappa_2\theta}\mathrm{F}_2+\mathrm{C}_3e^{i\kappa_3\theta}\mathrm{F}_3,$$

$$\Psi = \mathrm{C}e^{i\kappa\theta}\mathrm{G}+\mathrm{C}_1e^{i\kappa_1\theta}\mathrm{G}_1+\mathrm{C}_2e^{i\kappa_2\theta}\mathrm{G}_2+\mathrm{C}_3e^{i\kappa_3\theta}\mathrm{G}_3,$$

where C, C_1, C_2, C_3 are arbitrary constants, F, F_1, ..., G_2, G_3 are definite functions of period 2π, and κ, κ_1, κ_2, κ_3 are definite constants. When $\lambda = 0$, substituting in the equations

$$\Phi = e^{i\sigma\theta}, \quad \Psi = \mathrm{P}e^{i\sigma\theta},$$

we obtain

$$\sigma^2+p+2i\sigma\mathrm{P} = 0, \quad (\sigma^2+q)\,\mathrm{P}-2i\sigma = 0,$$

so that the values assumed by κ, κ_1, κ_2, κ_3, when $\lambda = 0$, are the roots of the equation

$$(\sigma^2+p)\,(\sigma^2+q)-4\sigma^2 = 0,$$

or

$$\sigma^4-\sigma^2+\tfrac{1}{4}m^2 = 0.$$

Thus

$$\sigma = \pm\,\{\tfrac{1}{2}\,(1+m)^{\frac{1}{2}} \pm (1-m)^{\frac{1}{2}}\},$$

and the four values are all imaginary when $m > 1$, and all real when $m < 1$. Supposing $\mathrm{S} > \mathrm{E} > \mathrm{M}$, we find at once, from the formula for m, that the least possible value of $\mathrm{S}/(\mathrm{S}+\mathrm{E}+\mathrm{M})$ in order that $m < 1$ is 0·96147..., but this requires M to be very small; but if $\mathrm{S}/(\mathrm{S}+\mathrm{E}+\mathrm{M})$ be greater than 0·9618..., then m is certainly < 1 even if $\mathrm{E} = \mathrm{M}$. In our solar system the sun's mass is more than 99·8 per cent. of the mass of the whole system; thus if S in our problem were the sun, and E, M were any two planets of the system, the condition for $m < 1$ would be easily satisfied. We shall then suppose $m < 1$.

Now compare with the equations (I.)″ the equations

$$\left.\begin{aligned}(1-2\lambda\cos\theta)\,(\Phi''-2\Psi') &= p\Phi,\\ (1-2\lambda\cos\theta)\,(\Psi''+2\Phi') &= q\Psi,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{III.})$$

obtained from (I.)″ by change of the sign of λ. They can also be obtained from (I.)″ by changing θ into $\theta+\pi$. This last change shows that the characteristic constants κ belonging to the equations (III.) are the same as for (I.)″, while the former change shows that the values of κ proper to (III.) are obtained by changing the sign of λ in the constants κ appropriate for (I.)″. When m is such that the values of κ for $\lambda = 0$, namely, the four values of σ above, are all different, a change in the sign of λ cannot interchange the values of κ among themselves. Thus we infer that each κ is unaltered by changing the sign of λ; for two of the values of σ can only be equal when $m^2 = 1$. In the applications in view of which the question was first considered, S denotes the sun, E denotes either Jupiter, or another planet such as Mercury, while M is of negligible mass. When E is Jupiter we have

$$m^2 = 27\tfrac{1}{1050}/(1+\tfrac{1}{1050})^2 = 0{\cdot}0257, \quad \lambda = \tfrac{1}{2}\,(0{\cdot}05) = 0{\cdot}025,$$

and m^2/λ is nearly unity. When E is mercury

$$m^2 = 27/5{\cdot}10^6 = 0{\cdot}0000054, \quad \lambda = \tfrac{1}{2}\,(0{\cdot}2) = 0{\cdot}1,$$

and $m^2 = 5{\cdot}4\lambda^6$, $m = (2{\cdot}3)\,\lambda^3$, nearly. In either case we may regard m as small, and the four possible values of σ are approximately

$$\pm\,(1-\tfrac{1}{8}m^2), \quad \pm\tfrac{1}{2}m,$$

of which the first two correspond to a period nearly the same but slightly greater than that of E, and the last two correspond to a period $\frac{2}{m}$ times that of E. When E is Jupiter, this last is $\frac{25}{2}$ times the period of Jupiter, or nearly 150 years; when E is Mercury, this period is approximately 200 years. As m is small we have approximately

$$p = 3-\tfrac{1}{12}m^2, \quad q = \tfrac{1}{12}m^2.$$

To neglect m^2 would be to neglect the ratio 27E/S; but we may remark in passing that if we put $q = 0$, $p = 3$, the equations give

$$\Psi'+2\Phi = \text{C, a constant,}$$

together with

$$\Phi''+\frac{1+8\lambda\cos\theta}{1+2\lambda\cos\theta}\Phi = 2\text{C},$$

of which the integration can be completed in finite terms. For it may be verified that the equation

$$(1+2\lambda\cos\theta)\,\Phi''+(1+8\lambda\cos\theta)\,\Phi = 0$$

possesses the two integrals

$$\sin\theta\,(1+2\lambda\cos\theta),$$

$$\cos\theta-2\lambda\,(1+\sin^2\theta)-4\lambda^2\cos\theta+8\lambda^3\cos 2\theta+12\lambda^2\sin\theta\,(1+2\lambda\cos\theta)\,\psi,$$

where

$$\psi = \int\frac{d\theta}{1+2\lambda\cos\theta}.$$

§ 8. We consider briefly, first of all, what would be the application of the method of infinite determinants to the equations (I.)$''$, which we may now write, with x, y for Φ, Ψ, in the forms

$$(1+2\lambda\cos\theta)\,(x''-2y') = px,$$

$$(1+2\lambda\cos\theta)\,(y''+2x') = qy.$$

We should substitute

$$x = \sum_{-\infty}^{\infty}\text{A}_n e^{i(\kappa+n)\theta}, \qquad y = \sum_{-\infty}^{\infty}\text{B}_n e^{i(\kappa+n)\theta},$$

and equate to zero the coefficients of the various powers of $e^{i\theta}$. The substitution gives, if $\zeta = e^{i\theta}$,

$$[1+\lambda\,(\zeta+\zeta^{-1})]\,\Sigma\,[\text{A}_n\,(\kappa+n)^2+2i\,(\kappa+n)\,\text{B}_n]\,\zeta^n+p\Sigma\text{A}_n\zeta^n = 0,$$

$$[1+\lambda\,(\zeta+\zeta^{-1})]\,\Sigma\,[\text{B}_n\,(\kappa+n)^2-2i\,(\kappa+n)\,\text{A}_n]\,\zeta^n+q\Sigma\text{B}_n\zeta^n = 0,$$

and, denoting $\kappa+n$ by κ_n, we obtain for the unknown coefficients A_n, B_n the equations

$$\lambda\,(\text{A}_{n-1}\kappa^2_{n-1}+2i\text{B}_{n-1}\kappa_{n-1})+\text{A}_n\,(\kappa_n^{\,2}+p)+2i\text{B}_n\kappa_n+\lambda\,(\text{A}_{n+1}\kappa^2_{n+1}+2i\text{B}_{n+1}\kappa_{n+1}) = 0,$$

$$\lambda\,(-2i\text{A}_{n-1}\kappa_{n-1}+\text{B}_{n-1}\kappa^2_{n-1})-2i\text{A}_n\kappa_n+\text{B}_n\,(\kappa_n^{\,2}+q)+\lambda\,(-2i\text{A}_{n+1}\kappa_{n+1}+\text{B}_{n+1}\kappa^2_{n+1}) = 0$$

If we now write

$$P_n = A_n\kappa_n^2 + 2iB_n\kappa_n, \qquad Q_n = -2iA_n\kappa_n + B_n\kappa_n^2,$$

which are equivalent with

$$A_n = \frac{\kappa_n P_n - 2iQ_n}{\kappa_n(\kappa_n^2-4)}, \qquad B_n = \frac{2iP_n + \kappa_n Q_n}{\kappa_n(\kappa_n^2-4)},$$

the equations may be replaced by

$$\left.\begin{aligned} \lambda P_{n-1} \qquad\quad + a_nP_n + b_nQ_n + \lambda P_{n+1} \qquad\quad &= 0, \\ \lambda Q_{n-1} + c_nP_n + d_nQ_n + \qquad\quad \lambda Q_{n+1} &= 0, \end{aligned}\right\} \quad . \quad . \quad . \quad (A)$$

wherein

$$a_n = 1 + \frac{p}{\kappa_n^2-4}, \qquad b_n = \frac{-2ip}{\kappa_n(\kappa_n^2-4)},$$

$$c_n = \frac{2iq}{\kappa_n(\kappa_n^2-4)}, \qquad d_n = 1 + \frac{q}{\kappa_n^2-4},$$

so that

$$a_nd_n - b_nc_n = \frac{\kappa_n^4 - \kappa_n^2 + \frac{1}{4}m^2}{\kappa_n^2(\kappa_n^2-4)},$$

it being remembered that $p+q = 3$, $pq = \frac{1}{4}m^2$.

When we eliminate $P_{n-1}, \ldots, Q_{n+1}$ from the equations (A), we obtain an infinite determinant, which, leaving aside questions of convergence, we may denote by

$$\left|\begin{array}{cccccccccccc}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \lambda & \cdot & a_{-1} & b_{-1} & \lambda & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \lambda & c_{-1} & d_{-1} & \cdot & \lambda & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \lambda & \cdot & a & b & \lambda & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \lambda & c & d & \cdot & \lambda & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \lambda & \cdot & a_1 & b_1 & \lambda & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \lambda & c_1 & d_1 & \cdot & \lambda & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot
\end{array}\right| = 0.$$

The product of the diagonal determinants $a_nd_n - b_nc_n$ is here

$$\frac{\sin\pi(\kappa-\sigma_1)\,.\,\sin\pi(\kappa-\sigma_2)\,.\,\sin\pi(\kappa-\sigma_3)\,.\,\sin\pi(\kappa-\sigma_4)}{\sin^4\pi\kappa},$$

where σ_1, σ_2, σ_3, σ_4 are the four roots of $\sigma^4 - \sigma^2 + \frac{1}{4}m^2 = 0$, previously considered. In using this determinant to obtain a further approximation to κ it would seem appropriate to use a theorem* for the expression of a determinant of $2n$ rows and columns as a Pfaffian, a sum $1 . 3 . 5 \ldots (2n-1)$ terms, of which each term is a product of n factors, each factor being of the form

$$(12) = a_1 b'_1 - a'_1 b_1 + a_2 b'_2 - a'_2 b_2 + \ldots + a_n b'_n - a'_n b_n,$$

where the elements

$$a_1 b_1,\ a_2 b_2,\ \ldots,\ a_n b_n,$$

$$a'_1 b'_1,\ a'_2 b'_2,\ \ldots\ a'_n b'_n,$$

are the constituents of two rows of the determinant. For in this case the factors (12) are easily calculated. But we do not pursue this method.

§ 9. Instead we proceed as follows. In the equations

$$[1+\lambda(\zeta+\zeta^{-1})]\,[x''-2y'] = px,$$

$$[1+\lambda(\zeta+\zeta^{-1})]\,[y''+2x'] = qy,$$

where $\zeta = e^{i\theta}$, write

$$x = e^{i\kappa\theta}\mathrm{X}, \qquad y = e^{i\kappa\theta}\mathrm{Y}, \qquad \kappa = \sigma + \kappa_2\lambda^2 + \kappa_4\lambda^4 + \ldots,$$

in which κ_2, κ_4, … are certain functions of p, q to be determined. Then the equations become

$$\left.\begin{array}{l}[1+\lambda(\zeta+\zeta^{-1})]\,[\mathrm{X}''-2\mathrm{Y}'+2i\kappa(\mathrm{X}'-\mathrm{Y})-\kappa^2\mathrm{X}] = p\mathrm{X}, \\ [1+\lambda(\zeta+\zeta^{-1})]\,[\mathrm{Y}''-2\mathrm{X}'+2i\kappa(\mathrm{Y}'+\mathrm{X})-\kappa^2\mathrm{Y}] = q\mathrm{Y},\end{array}\right\}$$

which by the general theory are capable of periodic solution when κ is properly chosen. Put then

$$\mathrm{X} = 1+\lambda\phi_1+\lambda^2\phi_2+\ldots, \qquad \mathrm{Y} = \mathrm{P}(1+\lambda\psi_1+\lambda^2\psi_2+\ldots),$$

where P is a constant; the differential equations then take the forms

$$(1+\lambda w)(\mathrm{H}_0+\lambda\mathrm{H}_1+\lambda^2\mathrm{H}_2+\ldots) = p\mathrm{X},$$

$$(1+\lambda w)(\mathrm{K}_0+\lambda\mathrm{K}_1+\lambda^2\mathrm{K}_2+\ldots) = q\mathrm{Y},$$

w denoting $\zeta+\zeta^{-1}$. Comparing the coefficients of like powers of λ,

$$\mathrm{H}_0 = p, \qquad \mathrm{K}_0 = \mathrm{P}_q, \qquad \mathrm{H}_1+w\mathrm{H}_0 = p\phi_1, \qquad \mathrm{K}_1+w\mathrm{K}_0 = q\mathrm{P}\psi_1,$$

and, in general,

$$\mathrm{H}_n+w\mathrm{H}_{n-1} = p\phi_n, \qquad \mathrm{K}_n+w\mathrm{K}_{n-1} = \mathrm{P}q\psi_n,$$

so that

$$\mathrm{H}_1 = p(\phi_1-w), \qquad \mathrm{K}_1 = \mathrm{P}q(\psi_1-w),$$

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* Proved in SCOTT-MATHEWS' 'Determinants' (1904), Chap. VIII, p. 99, § 19. Also in BAKER, 'Multiply-periodic Functions,' p. 314.

and, in general,

$$\mathrm{H}_n = p\,[\phi_n - w\phi_{n-1} + w^2\phi_{n-2} - \ldots + (-w)^n],$$

$$\mathrm{K}_n = \mathrm{P}q\,[\psi_n - w\psi_{n-1} + w^2\psi_{n-2} - \ldots + (-w)^n],$$

where H_n, K_n are the coefficients of λ^n respectively in

$$\mathrm{X}'' - 2\mathrm{Y}' + 2i\kappa\,(\mathrm{X}' - \mathrm{Y}) - \kappa^2\mathrm{X},$$

$$\mathrm{Y}'' + 2\mathrm{X}' + 2i\kappa\,(\mathrm{Y}' + \mathrm{X}) - \kappa^2\mathrm{Y}.$$

In particular

$$\mathrm{H}_0 = -2i\sigma\mathrm{P} - \sigma^2, \quad \mathrm{K}_0 = 2i\sigma - \sigma^2\mathrm{P},$$

so that

$$\sigma^2 + p + 2i\sigma\mathrm{P} = 0, \quad 2i\sigma = (\sigma^2 + q)\,\mathrm{P},$$

and, as previously,

$$\sigma^4 - \sigma^2 + \tfrac{1}{4}m^2 = 0,$$

while, if we write

$$\mathrm{P} = \frac{\sigma^2 + p}{-2i\sigma}, \quad \mathrm{Q} = \frac{\sigma^2 + q}{2i\sigma},$$

which are both pure imaginaries, we have $\mathrm{PQ} = 1$.

Next

$$\mathrm{H}_1 = \phi''_1 - 2\mathrm{P}\psi'_1 + 2i\sigma\,(\phi'_1 - \mathrm{P}\psi_1) - \sigma^2\phi_1,$$

$$\mathrm{K}_1 = \mathrm{P}\,[\psi''_1 + 2\mathrm{Q}\phi'_1 + 2i\sigma\,(\psi'_1 + \mathrm{Q}\phi_1) - \sigma^2\psi_1];$$

putting these respectively equal to $p\,(\phi_1 - w)$, $\mathrm{P}q\,(\psi_1 - w)$, we obtain two differential equations for ϕ_1 and ψ_1. If we assume

$$\phi_1 = \mathrm{A}_1\zeta + \mathrm{A}_{-1}\zeta^{-1}, \quad \psi_1 = \mathrm{B}_1\zeta + \mathrm{B}_{-1}\zeta^{-1},$$

and notice that

$$(\zeta^r)' = ir\zeta^r, \quad (\zeta^r)'' = -r^2\zeta^r,$$

we find, writing σ_n for $\sigma + n$,

$$\mathrm{A}_1\,(\sigma_1{}^2 + p) + 2\mathrm{P}i\sigma_1\mathrm{B}_1 = p, \qquad \mathrm{A}_{-1}\,(\sigma_{-1}{}^2 + p) + 2\mathrm{P}i\sigma_{-1}\mathrm{B}_{-1} = p,$$

$$-\mathrm{A}_1\,.\,2\mathrm{Q}i\sigma_1 + (\sigma_1{}^2 + q)\,\mathrm{B}_1 = q, \quad -\mathrm{A}_{-1}2\mathrm{Q}i\sigma_{-1} + (\sigma_{-1}{}^2 + q)\,\mathrm{B}_{-1} = q.$$

If

$$\Delta_1 = \sigma_1{}^4 - \sigma_1{}^2 + \tfrac{1}{4}m^2,$$

these give

$$\Delta_1\mathrm{A}_1 = (\sigma_1{}^2 + q)\,p + \frac{\sigma_1}{\sigma}(\sigma^2 + p)\,q,$$

$$\Delta_1\mathrm{B}_1 = (\sigma_1{}^2 + p)\,q + \frac{\sigma_1}{\sigma}(\sigma^2 + q)\,p,$$

with similar equations for A_{-1}, B_{-1}.

Proceeding similarly to equate terms in λ^2, we find

$$\phi''_2 + 2i\sigma\phi'_2 - \sigma^2\phi_2 - 2\mathrm{P}\,(\psi'_2 + i\sigma\psi_2) - 2\kappa_2\,(i\mathrm{P} + \sigma) = p\,(\phi_2 - w\phi_1 + w^2),$$

$$\psi''_2 + 2i\sigma\psi'_2 - \sigma^2\psi_2 + 2\mathrm{Q}\,(\phi'_2 + i\sigma\phi_2) - 2\kappa_2\,(-i\mathrm{Q} + \sigma) = q\,(\psi_2 - w\psi_1 + w^2).$$

If herein we assume

$$\phi_2 = A_2\zeta^2 + A_{-2}\zeta^{-2} + H, \quad \psi_2 = B_2\zeta^2 + B_{-2}\zeta^{-2} + K,$$

and equate terms in ζ^2, ζ^{-2}, ζ^0, we obtain

$$A_2(\sigma_2^2+p)+2Pi\sigma_2 B_2 = p(A_1-1), \qquad A_{-2}(\sigma^2_{-2}+p)+2Pi\sigma_{-2}B_{-2} = p(A_{-1}-1),$$

$$-A_2 \,.\, 2Qi\sigma_2+(\sigma_2^2+q)B_2 = q(B_1-1), \quad -A_{-2}\,.\,2Qi\sigma_{-2}+(\sigma^2_{-2}+q)B_{-2} = q(B_{-1}-1),$$

and

$$(\sigma^2+p)(H-K)+2\kappa_2(iP+\sigma) = p(A_1+A_{-1}-2),$$

$$-(\sigma^2+q)(H-K)+2\kappa_2(-iQ+\sigma) = q(B_1+B_{-1}-2),$$

wherein the coefficients of $H-K$ and κ_2 have for determinant

$$(\sigma^2+p)(-iQ+\sigma)+(\sigma^2+q)(iP+\sigma),$$

which is

$$\sigma(1-m^2)^{\frac{1}{2}}$$

and is not zero. That H, K should not be determinable separately is obvious *à priori;* to regard H as zero would be equivalent to dividing X, Y by a power series in λ^2 with constant coefficients. We notice that the successive coefficients A_1, A_{-1}, …, B_2, B_{-2} are all real. The value found for κ_2 is

$$\kappa_2 = pq\frac{7-6\sigma^2}{\sigma(1-2\sigma^2)(1-4\sigma^2)}.$$

A similar procedure can be continued. The differential equations for ϕ_3, ψ_3 can be solved by forms

$$\phi_3 = A_3\zeta^3+A_{-3}\zeta^{-3}+H_1\zeta+H_{-1}\zeta^{-1}, \quad \psi_3 = B_3\zeta^3+B_{-3}\zeta^{-3}+K_1\zeta+K_{-1}\zeta^{-1},$$

the differential equations for ϕ_4, ψ_4 by forms

$$\phi_4 = A_4\zeta^4+A_{-4}\zeta^{-4}+M_2\zeta^2+M_{-2}\zeta^{-2}+M,$$

$$\psi_4 = B_4\zeta^4+B_{-4}\zeta^{-4}+N_2\zeta^2+N_{-2}\zeta^{-2}+N,$$

and then the terms in ζ^0 will involve the unknown quantities

$$(\sigma^2+p)(M-N)+2\kappa_4(iP+\sigma),$$

$$-(\sigma^2+q)(M-N)+2\kappa_4(-iQ+\sigma),$$

from which κ_4 is found. And it serves as verification of the computation to see that κ_4 involves H, K only in the combination $H-K$, as it must in order to be determined without ambiguity.

The value found for x is of the form

$$x = e^{i\kappa\theta}[1+(\lambda\zeta, \lambda\zeta^{-1})+(\lambda^2\zeta^2, \lambda^2\zeta^{-2}, \lambda^2)+(\lambda^3\zeta^3, \lambda^3\zeta^{-3}, \lambda^3\zeta, \lambda^3\zeta^{-1})$$
$$+(\lambda^4\zeta^4, \lambda^4\zeta^{-4}, \lambda^4\zeta^2, \lambda^4\zeta^{-2}, \lambda^4)+\ldots],$$

or, say,

$$x = e^{i\kappa\theta}[u_0+\lambda\zeta u_1+\lambda\zeta^{-1}u_{-1}+\lambda^2\zeta^2 u_2+\lambda^2\zeta^{-2}u_{-2}+\ldots],$$

where every one of u_0, u_1, u_{-1}, u_2, u_{-2}, ... is a power series in λ^2 with real coefficients, not generally vanishing with λ^2. And similarly for y.

§ 10. The interesting case of the preceding solution is that corresponding to the value of σ given by

$$\sigma = \tfrac{1}{2}[(1+m)^{\frac{1}{2}}-(1-m)^{\frac{1}{2}}], \quad = \tfrac{1}{2}m\left(1+\frac{m^2}{8}+\ldots\right).$$

The quantity

$$\kappa_2 = pq\,\frac{7-6\sigma^2}{\sigma(1-2\sigma^2)(1-4\sigma^2)}$$

is then equal to

$$\tfrac{1}{2}m\left(7+\tfrac{65}{8}m^2\right)$$

approximately, and $\kappa_2\lambda^2$ is of the order $m\lambda^2$. When $m^2 \propto \lambda$, this is of the order m^5 or $\lambda^{5/2}$; when $m \propto \lambda^3$, it is of the order $m^{5/3}$ or λ^5. Thus a very few terms of the preceding solutions would seem to be sufficient for practical cases.

PART II.

§ 11. A large part of the interest of POINCARÉ'S 'Methodés Nouvelles de la Mécanique Céleste' depends on his criticism of the convergence of the series used by astronomers, particularly those series in which the time enters only under trigonometrical signs. In t. II., p. 277, he refers to a linear differential equation

$$\frac{d^2x}{dt^2}+x(1+\psi) = 0,$$

in which ψ, for our purposes, may be supposed to have a form

$$\psi = 4a\cos ht+4b\cos kt,$$

in which a, b are small. When h, k are commensurable the equation has periodic coefficients, and POINCARÉ makes the convergence of the series expressing the solution depend on this circumstance ('Méth. Nouv.,' t. I., p. 66). Considering the case in which h and k are incommensurable, and so ψ not periodic, and supposing a, b to have common a small factor μ, he obtains formal solutions of the differential equation in sines and cosines, and says "les séries . . ., qu'on peut ordonner suivant les puissances de μ, ne sont plus convergentes" ('Méth Nouv.,' t. II., pp. 277, 278). On the contrary, I believe that the solution of the differential equation above, arranged as a power series in a and b, converges for all finite values of these parameters, and that this is a consequence of a general theory of linear differential equations considered in papers* published by me in 1902. As this theory is capable of application to many other differential equations, as will be illustrated below by application to the equation considered by G. W. HILL for the motion of the moon's perigee, I wish to deal with it here, repeating the argument in part.

§ 12. Consider any system of linear differential equations, the n^2 coefficients

$$\frac{dx_i}{dt} = u_{i1}x_1 + \ldots + u_{in}x_n, \qquad (i = 1, 2, \ldots, n),$$

u_{ij} being functions of t. If these are considered only for real values of t, the properties which we require to assume are that, along a certain range which we shall suppose to include $t = 0$, these functions u_{ij} are single-valued, limited, and capable of integration, the same being true of certain other functions derived from these by multiplications, and further, that certain infinite series, which we shall prove to be absolutely and uniformly convergent, are capable of differentiation, term by term. But in the majority of practical cases the coefficients u_{ij} may be looked upon as the values, when t is real, of functions of a complex variable t. In this case we suppose a star region to be defined by lines passing to infinity from certain points in the finite part of the plane, which we call the singular points; we suppose $t = 0$ not to be a singular point, and the lines may be straight continuations of the radii joining the origin to these singular points. Within this star region, bounded by the lines in question, the functions u_{ij} are supposed to be single-valued and capable of development by power series about every point, forming monogenic analytic functions in the usual sense. Taking then any region within this star region, we obtain solutions of the differential equations, with arbitrary values for $t = 0$, in the form of infinite series of functions, obtained by quadratures, which are proved to converge absolutely and uniformly within the region taken.

The method of forming these solutions is extremely simple, involving only integrations and multiplications, but the way in which the work is arranged, though often of great utility, does not seem yet to find common acceptance, and some words must be given to it.

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* 'Proc. Lond. Math. Soc.,' XXXIV., 1902, p. 355; XXXV., 1902, p. 339. See also the same 'Proc.,' 2nd Series, II., p. 293, where it is explained that the same idea had already been used by PEANO and others. To me the method was independently suggested by the theory of continuous groups, 'Proc. Lond. Math. Soc.,' XXXIV., 1902, p. 91. POINCARÉ'S conclusions as to the convergence of astronomical series have been criticised by G. W. HILL, 'Coll. Works,' IV., p. 94; but the point there at issue is different from that considered here. In connexion with an example considered by POINCARÉ, *loc. cit.*, p. 279, see BRUNS, 'Astr. Nachr.,' No. 2606 (CIX., 1884), pp. 217, 218. Also BOREL, 'Théorie des Fonctions' (1898), p. 27; HARDY, 'Quart. Journ.,' XXXVI., p. 93; 'Proc. Lond. Math. Soc.,' III., p. 441, and the references there given.

The n^2 quantities u_{ij} can be arranged to form a square of n rows and n columns, the first suffix i denoting the row, and the second suffix j denoting the column in which a particular element u_{ij} is placed. This square is denoted by a single symbol, say u, and called a matrix. The symbol uv, formed from the two symbols u, v, written in a definite order, denotes then another matrix whose $(i, j)^{\text{th}}$ element has the value

$$u_{i1}v_{1j}+u_{i2}v_{2j}+\ldots+u_{in}v_{nj},$$

which is formed from the elements of the i^{th} *row* of the matrix u and those of the j^{th} *column* of the matrix v. This new matrix uv is called the product of u and v, taken in this order; it is generally different from vu. The symbol 1, when used for a matrix of an assigned number of rows and columns, denotes the matrix of which every element is zero except those in the diagonal, all of which have the same value, unity; it is easy to see that any matrix is unaltered by multiplication with the matrix unity of the same number of rows and columns. The symbol u^{-1} denotes the matrix such that the product $u^{-1}u$ is the matrix unity; in that case uu^{-1} is equal to $u^{-1}u$; the symbol u^{-1} is nugatory when the determinant formed with the elements of u is zero, and only then. In general, the determinant formed with the elements of u will be denoted by $|u|$. By the *sum*, $u+v$, of two matrices u, v, of the same number of rows and columns, is meant the matrix whose $(i, j)^{\text{th}}$ element is $u_{ij}+v_{ij}$, and, similarly, for the difference. Frequently we denote the aggregate of a row of n quantities, x_1, x_2, ..., x_n by the single letter x; then if u be a matrix of n rows and columns, the symbol ux denotes a set of n quantities of which the i^{th} is

$$u_{i1}x_1+u_{i2}x_2+\ldots+u_{in}x_n.$$

By the differential coefficient of a matrix we mean the single matrix whose elements are the differential coefficients of the given one. In what follows, if the $(i, j)^{\text{th}}$ element of a matrix u be a function of t, we denote by $\mathrm{Q}u$ the matrix of which the $(i, j)^{\text{th}}$ element is the integral of u_{ij} taken in regard to t from $t = 0$ to $t = t$. If, for an instant this matrix $\mathrm{Q}u$ be denoted by v, the product matrix uv will be denoted by $u\mathrm{Q}u$, and the matrix $\mathrm{Q}(uv)$, or $\mathrm{Q}(u\mathrm{Q}u)$, will be denoted by $\mathrm{Q}u\mathrm{Q}u$. Similarly, $\mathrm{Q}(u \,.\, \mathrm{Q}u\mathrm{Q}u)$ will be denoted by $\mathrm{Q}u\mathrm{Q}u\mathrm{Q}u$, and so on.

Now consider a matrix of which the $(i, j)^{\text{th}}$ element is the infinite series formed by the sum of the $(i, j)^{\text{th}}$ elements taken from the matrix unity (of the same number of rows and columns as u), the matrix $\mathrm{Q}u$, the matrix $\mathrm{Q}u\mathrm{Q}u$, the matrix $\mathrm{Q}u\mathrm{Q}u\mathrm{Q}u$, and so on. This will be denoted by

$$\Omega(u) = 1+\mathrm{Q}u+\mathrm{Q}u\mathrm{Q}u+\mathrm{Q}u\mathrm{Q}u\mathrm{Q}u+\ldots,$$

and the series on the right will be said to be uniformly and absolutely convergent when this property is proved to hold for each of the n^2 infinite series which constitute its elements.

Repeating now the demonstration given, 'Proc. Lond. Math. Soc.,' April 10, 1902, p. 354, let $u_{ij}^{(1)}$ denote the $(i, j)^{\text{th}}$ element of the matrix Qu, that is,

$$u_{ij}^{(1)} = \int_0^t u_{ij}\, dt\,;$$

similarly, let $u_{ij}^{(2)}$ denote the $(i, j)^{\text{th}}$ element of the matrix $QuQu$, namely,

$$u_{ij}^{(2)} = \int_0^t \left[u_{i1}u_{1j}^{(1)} + u_{i2}u_{2j}^{(1)} + \ldots + u_{in}u_{nj}^{(1)}\right] dt,$$

and so on. For the region chosen within the star region above explained, when the functions u_{ij} are functions of a complex variable, or for the range of values of t adopted when the elements u_{ij} are functions of a real variable, there will exist a real positive quantity M_{ij} not exceeded by the absolute value of u_{ij} for the values of t involved. Taking a path of integration limited to such values, from the origin $t = 0$ to $t = t$, this being a rectifiable curve of length s, let t_1 be an intermediate point of this path, the length of the path from the origin to t_1 being s_1. Then we have, considering absolute values,

$$|u_{ij}^{(1)}(t)| \leqq M_{ij} \int_0^s ds_1 \leqq sM_{ij},$$

and in particular

$$|u_{ij}^{(1)}(t_1)| \leqq s_1 M_{ij}.$$

Similarly,

$$|u_{ij}^{(2)}(t)| \leqq \int_0^s (M_{i1}s_1M_{1j} + \ldots + M_{in}s_1M_{nj})\, ds_1\,;$$

now if M denote the matrix whose $(i, j)^{\text{th}}$ element is M_{ij}, the $(i, j)^{\text{th}}$ element of the matrix M^2, formed by the product of M with itself, will be

$$M_{i1}M_{1j} + M_{i2}M_{2j} + \ldots + M_{in}M_{nj},$$

which we may denote by $(M^2)_{ij}$; thence

$$|u_{ij}^{(2)}(t)| \leqq (M^2)_{ij} \int_0^s s_1\, ds_1 \leqq \tfrac{1}{2}s^2 (M^2)_{ij},$$

and in particular

$$|u_{ij}^{(2)}(t_1)| \leqq \tfrac{1}{2}s_1^2 (M^2)_{ij}.$$

We can continue this process. The next step will be

$$|u_{ij}^{(3)}(t)| \leqq \int_0^s \tfrac{1}{2}s_1^2\, ds_1 \left[M_{i1}(M^2)_{1j} + \ldots + M_{in}(M^2)_{nj}\right],$$

$$\leqq \frac{s^3}{3\,!}(M^3)_{ij}.$$

Thus we see that each of the n^2 infinite series constituting the elements of the matrix

$$\Omega(u) = 1 + Qu + QuQu + \ldots$$

has terms whose moduli are respectively equal to, or less than, the real positive terms of the corresponding infinite series constituting the elements of the matrix

$$1 + sM + \frac{s^2}{2!}M^2 + \frac{s^3}{3!}M^3 + \ldots.$$

This last is, however, certainly convergent for all finite values of s, whatever be the (finite) values of the elements of the matrix M. For the case when the algebraic equation satisfied by M has unequal roots, its sum is given by the formula of 'Proc. Lond. Math. Soc.,' XXXIV., February 14, 1901, p. 114, which can be easily modified to meet the case of unequal roots.

Thus each of the elements of the matrix $\Omega(u)$ is an absolutely and uniformly convergent series; in the case when the elements u_{ij} are functions of the complex variable, as explained above, it follows that every element of the matrix $\Omega(u)$ is a function of the complex variable, and differentiation (and integration) of the series representing this element is permissible, term by term. For the case of real functions we introduce this as a condition.

Hence, if x^0 denote a row of n arbitrary values $x_1^0, x_2^0, \ldots, x_n^0$, the row of n quantities denoted by

$$x = \Omega(u)x^0$$

is at once seen to form a set of n integrals of the differential equations, reducing for $t = 0$ to the arbitrary values x^0, that is, x_i reducing to x_i^0. For if v denote any matrix, of n rows and columns, whose elements are differentiable functions of t, if x^0 denote a row of n constants, and y the set of n functions given by

$$y = vx^0,$$

that is,

$$y_i = v_{i1}x_1^0 + v_{i2}x_2^0 + \ldots + v_{in}x_n^0,$$

we have

$$\frac{dy_i}{dt} = \frac{dv_{i1}}{dt}x_1^0 + \ldots + \frac{dv_{in}}{dt}x_n^0,$$

which, if $\frac{dv}{dt}$ denote the matrix whose elements are the differential coefficients of the elements of v, we can denote by

$$\frac{dy}{dt} = \frac{dv}{dt}x^0.$$

Hence the equation

$$x = \Omega(u)x^0,$$

gives

$$\begin{aligned}\frac{dx}{dt} &= \frac{d}{dt}(1+\mathrm{Q}u+\mathrm{Q}u\mathrm{Q}u+\ldots)\,x^0,\\ &= \frac{d}{dt}[1+\mathrm{Q}u+\mathrm{Q}(u\mathrm{Q}u)+\mathrm{Q}(u\mathrm{Q}u\mathrm{Q}u)+\ldots]\,x^0,\\ &= [u+u\mathrm{Q}u+u\mathrm{Q}u\mathrm{Q}u+\ldots]\,x^0,\\ &= u\,[1+\mathrm{Q}u+\mathrm{Q}u\mathrm{Q}u+\ldots]\,x^0,\\ &= u\Omega(u)\,x^0,\end{aligned}$$

or

$$dx/dt = ux,$$

so that the functions $x = \Omega(u)\,x^0$ satisfy the differential equations. By the definition, $\mathrm{Q}u_{ij}$ reduces to zero for $t = 0$; hence $\Omega(u)$ reduces to its first term, the matrix unity, when $t = 0$; that is, $x = \Omega(u)\,x^0$ reduces to $x = x^0$ when $t = 0$.

In what follows we shall require a particular property of the matrix $\Omega(u)$, given in 'Proc. Lond. Math. Soc.,' XXXV., December 11, 1902, p. 339. If u, v be any two matrices of n rows and columns, of similar character to the u considered above, the property is expressed by

$$\Omega(u+v) = \Omega(u)\,\Omega\,\{[\Omega(u)]^{-1}\,v\Omega(u)\},$$

where $[\Omega(u)]^{-1}$ is the matrix inverse to $\Omega(u)$, defined above, such that $[\Omega(u)]^{-1}\,\Omega(u) = 1$. The theorem is nugatory when the determinant of $\Omega(u)$ is zero. It is only equivalent to saying that if in the system of linear differential equations

$$\frac{dx}{dt} = (u+v)\,x,$$

that is,

$$\frac{dx_i}{dt} = (u_{i1}+v_{i1})\,x_1+\ldots+(u_{in}+v_{in})\,x_n,$$

we introduce a set of n new dependent variables, denoted by z, by means of the equations

$$x = \Omega(u)\,z, \quad \text{or} \quad z = [\Omega(u)]^{-1}\,x,$$

then

$$dz/dt = [\Omega(u)]^{-1}\,v\Omega(u)\,z.$$

This follows at once from

$$\begin{aligned}(u+v)\,x = \frac{dx}{dt} = \frac{d}{dt}[\Omega(u)\,z] &= \left[\frac{d}{dt}\,\Omega(u)\right]z+\Omega(u)\,\frac{dz}{dt}\\ &= [u\Omega(u)]\,z+\Omega(u)\,\frac{dz}{dt} = u\Omega(u)\,z+\Omega(u)\,\frac{dz}{dt}\\ &= ux+\Omega(u)\,\frac{dz}{dt},\end{aligned}$$

which gives

$$\Omega(u)\frac{dz}{dt} = vx = v\Omega(u)z.$$

In what follows we shall generally write $\Omega^{-1}(u)$ in place of $[\Omega(u)]^{-1}$.

Another property to be noticed* is that the determinant of the matrix $\Omega(u)$ is equal to the exponential of the sum of the integrals from 0 to t of the diagonal elements of the matrix u. For, if Ω_{ij} denote the general element of $\Omega(u)$, the equation

$$\frac{d}{dt}\Omega(u) = u\Omega(u),$$

already remarked, is the aggregate of the equations

$$\frac{d\Omega_{ij}}{dt} = u_{i1}\Omega_{1j} + \ldots + u_{in}\Omega_{nj}.$$

Further, the differential coefficient of a determinant of n rows and columns can be written as a sum of n determinants, each of which is obtained from the original determinant by replacing the elements of one row respectively by their differential coefficients. Hence we at once see that, if Δ denote the determinant of $\Omega(u)$,

$$d\Delta/dt = (u_{11}+u_{22}+\ldots+u_{nn})\Delta,$$

which establishes the result in question.

In particular, if the sum of the diagonal elements of u,

$$u_{11}+u_{22}+\ldots+u_{nn},$$

be zero, the determinant of $\Omega(u)$ is independent of t, and is thus equal to unity. This result is of frequent application.

§ 13. After these introductory remarks we may at once show that the equation

$$\frac{d^2x}{dt^2} + x(1+4a\cos ht+4b\cos kt) = 0,$$

to which reference has been made, is capable of solution as an absolutely and uniformly converging series in a, b, whatever h and k may be. It will be as simple, and of utility for other applications we wish to make, to take the equation

$$\frac{d^2x}{dt^2} + x(n^2+\psi) = 0,$$

in which we may suppose n to be an integer.

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* *Cf.* DARBOUX, 'Compt. Rend.,' XC. (1880), p. 526.

In this last equation, put

$$\mathrm{X} = \tfrac{1}{2}e^{int}\left(\frac{dx}{dt}-inx\right), \qquad \mathrm{Y} = \tfrac{1}{2}e^{-int}\left(\frac{dx}{dt}+inx\right),$$

leading to

$$-inx = \mathrm{X}e^{-int}-\mathrm{Y}e^{int}, \qquad dx/dt = \mathrm{X}e^{-int}+\mathrm{Y}e^{int};$$

then we have

$$\frac{d\mathrm{X}}{dt} = -\frac{i\psi}{2n}\,e^{int}\,(\mathrm{X}e^{-int}-\mathrm{Y}e^{int}),$$

$$\frac{d\mathrm{Y}}{dt} = -\frac{i\psi}{2n}\,e^{-int}\,(\mathrm{X}e^{-int}-\mathrm{Y}e^{int}).$$

Writing

$$2it = \tau, \quad \zeta = e^{\tau},$$

these are

$$\frac{d\mathrm{X}}{d\tau} = -\frac{\psi}{4n}\,(\mathrm{X}-\mathrm{Y}\zeta^{n}), \quad \frac{d\mathrm{Y}}{d\tau} = -\frac{\psi}{4n}\,(\mathrm{X}\zeta^{-n}-\mathrm{Y}),$$

or, say,

$$\frac{d}{d\tau}(\mathrm{X}, \mathrm{Y}) = -\frac{\psi}{4n}\begin{pmatrix} 1, & -\zeta^{n} \\ \zeta^{-n}, & -1 \end{pmatrix}(\mathrm{X}, \mathrm{Y}),$$

where, as is usual, the single quantity $-\frac{\psi}{4n}$, written before the matrix, is to be multiplied into every element of the matrix.

In particular, when $n = 1$, $\psi = 4a\cos ht+4b\cos kt$,

$$\frac{d}{d\tau}(\mathrm{X}, \mathrm{Y}) = (ap+bq)\,(\mathrm{X}, \mathrm{Y}),$$

where p, q denote the matrices

$$p = \tfrac{1}{2}(\zeta^{\frac{1}{2}h}+\zeta^{-\frac{1}{2}h})\begin{pmatrix} -1, & \zeta \\ -\zeta^{-1}, & 1 \end{pmatrix}, \quad q = \tfrac{1}{2}(\zeta^{\frac{1}{2}k}+\zeta^{-\frac{1}{2}k})\begin{pmatrix} -1, & \zeta \\ -\zeta^{-1}, & 1 \end{pmatrix}.$$

Thus the solution is expressed by

$$(\mathrm{X}, \mathrm{Y}) = \Omega\,(ap+bq)\,(\mathrm{X}^{0}, \mathrm{Y}^{0}),$$

where $\Omega\,(ap+bq)$ is of the form

$$1+a\mathrm{Q}p+b\mathrm{Q}q+a^{2}\mathrm{Q}p\mathrm{Q}p+ab\,(\mathrm{Q}p\mathrm{Q}q+\mathrm{Q}q\mathrm{Q}p)+b^{2}\mathrm{Q}q\mathrm{Q}q+\ldots,$$

and we have proved that this series is uniformly and absolutely convergent.

If we assume such a form of solution it is easy by successive steps to obtain the values of the coefficients independently of the method we have adopted. What is of present importance is that we have shown the series to be convergent, a fact which appears to be denied by POINCARÉ.

§ 14. Leaving aside this point, we pass on now to the application of the general method here explained to the computation of the integrals of particular differential equations with periodic coefficients, as, for instance, the equation for the motion of the lunar perigee, considered by G. W. HILL.

It is known from the general theory that the solutions of the n equations

$$dx_i/dt = u_{i1}x_1 + \ldots + u_{1n}x_n, \quad (i = 1, 2, \ldots, n),$$

in which $u_{i1}, \ldots, u_{in}$ are single-valued functions with a common period, say w, can be written, in the most general case, in the forms

$$x_i = A_1 e^{\lambda_1 t}\phi_{i1} + \ldots + A_n e^{\lambda_n t}\phi_{in},$$

wherein $A_1, \ldots, A_n$ are arbitrary constants, $\lambda_1, \ldots, \lambda_n$ are n definite constants, and the functions ϕ_{ij} are n^2 definite functions all with the period w. In many applications it is the constants $\lambda_1, \ldots, \lambda_n$ which it is of most importance to find; when these are all pure imaginaries, the motion* represented by the differential equations presents, beyond the fundamental period w, secondary oscillations of periods $2\pi/i\lambda_r$, and the motion is conventionally said to be stable.

We show first how this form of solution naturally arises from the point of view we have adopted.

Write $\Omega_0^t(u)$ in place of $\Omega(u)$, and for simplicity write only two rows and columns of the matrix, though the argument is quite general. Make the limitation, which, as is well known, does not cover all cases, that there exists a matrix of constants, h, of n rows and columns, whose inverse is denoted by h^{-1}, such that the complete matrix $\Omega_0^w(u)$ can be written in the form

$$\Omega_0^w(u) = h \begin{pmatrix} e^{ic_1 w}, & 0 \\ 0, & e^{ic_2 w} \end{pmatrix} h^{-1}$$

with only diagonal elements, here denoted by $e^{ic_1 w}$, $e^{ic_2 w}$, in the reduced matrix. This will be so, in the technical phraseology, if the matrix $\Omega_0^w(u)$ has linear invariant factors.† Then, from the definition of $\Omega(u)$,

$$\Omega_0^{w+t}(u) = \Omega_w^{w+t}(u) \,.\, \Omega_0^w(u),$$

while, as u has period w,

$$\Omega_w^{w+t}(u) = \Omega_0^t(u).$$

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[*] Interesting physical examples are given by Lord RAYLEIGH, 'Collected Works,' III., p. 1.

[†] A proof of the general theorem for the reduction of a matrix, valid when this is of vanishing determinant, is given, 'Proc. Camb. Phil. Soc.,' XII. (1903), p. 65. The literature of this matter, which begins with SYLVESTER, 'Coll. Papers,' I., pp. 119, 139, 219, and WEIERSTRASS, 'Ges. Werke,' I., p. 233, is very wide. The reader may consult MUTH, 'Elementartheiler,' Leipzig, 1899.

Hence

$$\Omega_0^{w+t}(u) \, . \, h = \Omega_0^{t}(u) \, . \, h \begin{pmatrix} e^{ic_1 w}, & 0 \\ 0, & e^{ic_2 w} \end{pmatrix} h^{-1},$$

and so

$$\Omega_0^{w+t}(u) \, . \, h \begin{pmatrix} e^{-ic_1(w+t)}, & 0 \\ 0, & e^{-ic_2(w+t)} \end{pmatrix} = \Omega_0^{t}(u) \, . \, h \begin{pmatrix} e^{-ic_1 t}, & 0 \\ 0, & e^{-ic_2 t} \end{pmatrix}.$$

This shows that the matrix on the right has period w. Put then

$$\mathrm{P}_0^{t} = \Omega_0^{t}(u) \, h \begin{pmatrix} e^{-ic_1 t}, & 0 \\ 0, & e^{-ic_2 t} \end{pmatrix} h^{-1},$$

which has period w, and is such that $\mathrm{P}_0^{w} = \mathrm{P}_0^{0} = 1$. The matrix $\Omega_0^{t}(u)$ can therefore be written in the form

$$\Omega_0^{t}(u) = \mathrm{P}_0^{t} \, . \, h \begin{pmatrix} e^{ic_1 t}, & 0 \\ 0, & e^{ic_2 t} \end{pmatrix} h^{-1},$$

which is the theorem in question.

We now compare this with the form of solution of the original differential equations by the method of successive approximation followed by LAGRANGE, LAPLACE, and others. We have

$$\begin{pmatrix} e^{ic_1 t}, & 0 \\ 0, & e^{ic_2 t} \end{pmatrix} = 1 + it \begin{pmatrix} c_1, & 0 \\ 0, & c_2 \end{pmatrix} + \frac{(it)^2}{2\,!} \begin{pmatrix} c_1^2, & 0 \\ 0, & c_2^2 \end{pmatrix} + \ldots\,;$$

thus

$$\Omega_0^{t}(u) = \mathrm{P}_0^{t} + t\mathrm{P}\,(h\gamma h^{-1}) + \frac{t^2}{2\,!}\mathrm{P}\,(h\gamma^2 h^{-1}) + \ldots,$$

where P is written for P_0^{t}, and γ is written for

$$\begin{pmatrix} ic_1, & 0 \\ 0, & ic_2 \end{pmatrix}.$$

If then, as in LAPLACE, 'Méc. Cél.,' Liv. II., Ch. V., t. I., of the edition of 1878. p. 266, we obtain the solutions of the differential equations in the form

$$(\mathrm{P}_0^{t} + t\mathrm{A} + t^2\mathrm{B} + \ldots)\, x^0,$$

where A, B are certain periodic matrices, and x^0 is a row of arbitrary constants, *we can obtain the constants* ic_1, ic_2, *which are the most important quantities in many applications, by taking the matrix* A, *which arises as the coefficient of* t, *and is equal in our notation to*

$$\mathrm{P}_0^{t}\,(h\gamma h^{-1}),$$

putting therein $t = 0$, *so obtaining, say* A_0, *equal in our notation to* $h\gamma h^{-1}$, *and then solving the determinantal equation*

$$|A_0-\lambda| = 0,$$

whose roots are ic_1 *and* ic_2. This process will be found to be equivalent to the general procedure explained by LAPLACE, in the passage above referred to, for bringing the time under trigonometrical signs. We have considered only the case of linear differential equations with periodic coefficients, and have supposed $\Omega_0^w(u)$ to have linear invariant factors; LAPLACE'S method, if less definite, is of much wider application. An interesting exposition of the method in general is given by M. O. CALLANDREAU, 'Ann. de l'Observ. de Paris,' XXII., 1896, pp. 16, 20.

We may notice that

$$A_0 = h\begin{pmatrix} ic_1, & 0 \\ 0, & ic_2 \end{pmatrix}h^{-1}$$

gives

$$\Omega(A_0) = h\begin{pmatrix} e^{ic_1t}, & 0 \\ 0, & e^{ic_2t} \end{pmatrix}h^{-1},$$

so that we also have

$$\begin{aligned}\Omega(u) &= P_0^t \,.\, \Omega(A_0) \\ &= P_0^t(1+tA_0+\tfrac{1}{2}t^2A_0^2+\ldots),\end{aligned}$$

and the quantities e^{ic_1w}, e^{ic_2w} are the roots of the equation

$$|\Omega_0^w(u)-\rho| = 0.$$

§ 15. When the sum of the diagonal elements of the matrix u is zero, the determinant of $\Omega(u)$ is unity, as above remarked. In this case, when $n = 2$, the two quantities e^{ic_1w}, e^{ic_2w} are inverses and $c_2 = -c_1$. In this case the equation

$$|\Omega_0^w(u)-\rho| = 0$$

gives at once the value of $\cos cw$. This appears, however, a less advantageous way of determining c_1, c_2 than that explained above, as requiring greater approximation in the calculation of $\Omega_0^t(u)$, as will be seen in examples.

The fact that c_1, c_2 are equal and of opposite signs is a particular case of a well-known theorem for the variational equations arising in the general dynamical case, which is proved by POINCARÉ ('Méth. Nouv.,' I., 193). The following proof, though longer, appears more fundamental in character. The general dynamical equations being

$$\frac{dx_r}{dt} = \frac{\partial F}{\partial y_r}, \qquad \frac{dy_r}{dt} = -\frac{\partial F}{\partial x_r},$$

where it will be sufficient to suppose r to have the values 1, 2; let

$$x_r = \phi_r(t), \qquad y_r = \psi_r(t),$$

be a solution of these equations. Substitute in the differential equations

$$x_r = \phi_r(t)+\xi_r, \qquad y_r = \psi_r(t)+\eta_r,$$

and retain only first powers of the quantities ξ_r and η_r, which are supposed to be small. We thence obtain a system of linear differential equations of the form

$$\left(\frac{d\xi_1}{dt}, \frac{d\eta_1}{dt}, \frac{d\xi_2}{dt}, \frac{d\eta_2}{dt}\right) = \beta^{-1}A(\xi_1, \eta_1, \xi_2, \eta_2),$$

where β is the skew-symmetrical matrix of constants given by

$$\beta = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

(so that $\beta^{-1} = -\beta$), and A is a symmetrical matrix whose elements are functions of t. We then have the theorems following:—

(a) The roots of the determinantal equation for λ,

$$|\beta^{-1}A-\lambda| = 0,$$

fall into pairs of equal roots of opposite sign;

(b) The determinantal equation for ρ,

$$|\Omega(\beta^{-1}A)-\rho| = 0,$$

is a reciprocal equation, unaltered by changing ρ into ρ^{-1}.

To express the proof we require a notation for the matrix obtained from a given matrix u by interchanging its rows with its columns, thus placing the element u_{ij} in the $(j, i)^{\text{th}}$ instead of the $(i, j)^{\text{th}}$ place. This transposed matrix may be denoted by trs (u) or by $\bar{u}$. It is easy also to show that

$$[\Omega(u)]^{-1} = \text{trs}\,[\Omega(-\bar{u})].$$

Then (a) is immediate from the obvious relations among determinants expressed by

$$|A-\beta\lambda| = |\bar{A}-\bar{\beta}\lambda| = |A+\beta\lambda|,$$

since $\bar{A} = A$, $\bar{\beta} = -\beta$.

For (*b*), since

$$\beta\Omega(u)\beta^{-1} = \Omega(\beta u\beta^{-1}), \qquad \text{trs}\,(\beta^{-1}\mathrm{A}) = -\mathrm{A}\beta^{-1},$$

we have the following transformations of matrices

$$[\Omega(\beta^{-1}\mathrm{A})]^{-1} = \text{trs}\,[\Omega(\mathrm{A}\beta^{-1})] = \text{trs}\,[\beta\Omega(\beta^{-1}\mathrm{A})\beta^{-1}] = \beta^{-1}[\text{trs}\,\Omega(\beta^{-1}\mathrm{A})]\,\beta,$$

and hence, writing $\Omega^{-1}(u)$ for $[\Omega(u)]^{-1}$, the following equations among determinants

$$|\Omega^{-1}(\beta^{-1}\mathrm{A})-\rho| = |\text{trs}\,\Omega(\beta^{-1}\mathrm{A})-\rho| = |\Omega(\beta^{-1}\mathrm{A})-\rho|,$$

which establishes the result in question.

§ 16. In many dynamical applications the matrix A is a sum of two matrices

$$\mathrm{A} = \alpha+\vartheta,$$

where α is a symmetrical matrix of real constants, and ϑ a symmetrical matrix whose elements are small. Suppose, further, that p, denoting a row of $2n$ real variables $p_1, p_2, \ldots$, the matrix α is such that the quadratic form

$$\Sigma\Sigma\alpha_{ij}p_ip_j$$

does not vanish unless every one of the $2n$ elements of p is zero, which requires that the determinant $|\alpha|$ is not zero. Then, if this quadratic form be denoted by αp^2, and if each of ξ and η be a row of $2n$ real quantities, the form

$$\alpha(\xi+i\eta)(\xi-i\eta), \quad = \alpha\xi^2+i\alpha(\eta\xi-\xi\eta)+\alpha\eta^2, \quad = \alpha(\xi^2+\eta^2),$$

has the same property.

When this is so, it can be shown that the roots of the determinantal equation in ψ,

$$|\beta^{-1}\alpha-\psi| = 0,$$

are pure imaginaries, and that the invariant factors of the matrix $\beta^{-1}\alpha-\psi$ are linear. As the proof is not long it may be given here (*cf.* 'Proc. Lond. Math. Soc.,' XXXV., December 11, 1902, p. 380).

Let ψ satisfy the determinantal equation

$$|\alpha-\beta\psi| = 0\,;$$

as the determinant $|\alpha|$ is not zero, ψ cannot be zero. Then $2n$ quantities $x_1, x_2, \ldots$, whose aggregate is denoted by x, can be taken to satisfy the $2n$ linear equations

$$(\alpha-\beta\psi)x = 0.$$

If x_0 denote the row formed by the $2n$ quantities which are the conjugate complexes of those of x, we have in turn

$$\alpha xx_0 = \psi\beta xx_0, \qquad \bar{\alpha}x_0x = \psi\bar{\beta}x_0x, \qquad \alpha x_0x = -\psi\beta x_0x,$$

and, therefore, ψ_0 being the conjugate complex of ψ

$$\alpha x x_0 = -\psi_0 \beta x x_0.$$

Hence

$$\left(\frac{1}{\psi}+\frac{1}{\psi_0}\right) \alpha x x_0 = 0,$$

showing that $\psi+\psi_0 = 0$, which proves that ψ is a pure imaginary.

Writing λ for ψ^{-1}, the equations above are the same as

$$(\alpha^{-1}\beta-\lambda) x = 0\,;$$

we prove that the invariant factors are linear by showing* that it is not possible to find a row of $2n$ quantities $y_1, y_2, \ldots$, such that

$$(\alpha^{-1}\beta-\lambda) y = x.$$

For this would involve

$$(\beta-\alpha\lambda) y x_0 = \alpha x x_0,$$

of which the right side is real, so that, λ being a pure imaginary, either of these would be equal to

$$(\beta+\alpha\lambda) y_0 x\,; \quad = (\bar{\beta}+\bar{\alpha}\lambda) x y_0 = (-\beta+\alpha\lambda) x y_0,$$

of which the last is zero in virtue of

$$(\alpha^{-1}\beta-\lambda) x = 0.$$

As $\alpha x x_0$ is not zero; the assumed equation for y is impossible, and the invariant factors are linear.

From this fact it follows that it is possible to find a matrix h such that

$$h^{-1}\beta^{-1}\alpha h = \begin{pmatrix} i\sigma_1 & 0 & 0 & 0 \\ 0 & -i\sigma_1 & 0 & 0 \\ 0 & 0 & i\sigma_2 & 0 \\ 0 & 0 & 0 & -i\sigma_2 \end{pmatrix},$$

where σ_1, σ_2 are real. Then the given differential equations, which are of the form

$$\left(\frac{d\xi_1}{dt}, \frac{d\eta_1}{dt}, \frac{d\xi_2}{dt}, \frac{d\eta_2}{dt}\right) = (\beta^{-1}\alpha+\beta^{-1}\vartheta)(\xi_1, \eta_1, \xi_2. \eta_2),$$

if transformed by the linear substitution

$$(\xi_1, \eta_1, \xi_2, \eta_2) = h\,(\mathrm{X}_1, \mathrm{Y}_1, \mathrm{X}_2, \mathrm{Y}_2)$$

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* See, for example, 'Proc. Camb. Phil. Soc.,' XII. (1903), p. 65.

take the forms

$$\left(\frac{dX_1}{dt},\ \frac{dY_1}{dt},\ \frac{dX_2}{dt},\ \frac{dY_2}{dt}\right) = (\sigma+\Theta)\,(X_1,\ Y_1,\ X_2,\ X_2),$$

where σ denotes the matrix above written, with only diagonal elements $i\sigma_1$, &c., and Θ is the matrix

$$\Theta = h^{-1}\beta^{-1}\vartheta h.$$

The solutions of these equations are then expressed by

$$(X_1,\ Y_1,\ X_2,\ Y_2) = \Omega\,(\sigma+\Theta)\,(X_1^0,\ Y_1^0,\ X_2^0,\ Y_2^0),$$

where X_1^0, Y_1^0, …, are the initial values. Now, by a previously given formula,

$$\Omega\,(\sigma+\Theta) = \Omega\,(\sigma)\,\Omega\,[\Omega^{-1}\,(\sigma)\,\Theta\Omega\,(\sigma)],$$

where $\Omega\,(\sigma)$ has the simple form

$$\Omega\,(\sigma) = \begin{pmatrix} e^{i\sigma_1 t} & 0 & 0 & 0 \\ 0 & e^{-i\sigma_1 t} & 0 & 0 \\ 0 & 0 & e^{i\sigma_2 t} & 0 \\ 0 & 0 & 0 & e^{-i\sigma_2 t} \end{pmatrix};$$

the solution is thereby expressed in powers of the small quantities occurring in ϑ.

The preceding work has wide applications; a particular case is that of the oscillations of a dynamical system about a state of steady motion, for which ϑ, and Θ, is zero.

[*October 30, 1915.*—To prevent misunderstanding, two remarks may be added to § 16. The condition that the quadratic form αx^2 should be positive, though sufficient, is not necessary in order that the roots of the determinantal equation $(\beta^{-1}\alpha-\psi) = 0$ should be pure imaginaries. For instance, if a, b, u, v be real positive constants, and H be a quadratic form

$$H = \tfrac{1}{2}a\,(y_1-nx_2)^2+\tfrac{1}{2}b\,(y_2-mx_1)^2-\frac{u^2}{2a}\,x_1^{\,2}-\frac{v^2}{2b}\,x_2^{\,2},$$

the motion about $x_1 = 0$, $x_2 = 0$, $y_1 = 0$, $y_2 = 0$ expressed by the equations

$$\dot{x}_1 = \partial H/\partial y_1,\quad \dot{y}_1 = -\partial H/\partial x_1,\quad \dot{x}_2 = \partial H/\partial y_2,\quad \dot{y}_2 = -\partial H/\partial x_2,$$

is instantaneously stable if $ab\,(m-n)^2 > (u+v)^2$, the corresponding quartic equation having all its roots purely imaginary. This essentially is the case noticed by THOMSON and TAIT, 'Natural Philosophy,' I., pp. 395, 398, where the illustration is that of a gyrostat balanced on gimbals. A simple illustration is also that of the oscillations about steady motion of a weight suspended by a string of which the other end is made to describe uniformly a horizontal circle, in the case in which the string intersects the vertical drawn *downwards* from the centre of the circle described by its upper end. This motion is not, however, secularly stable when there is Dissipativity (THOMSON and TAIT, as above, p. 388); and, of course, not instantaneously stable, the roots of the corresponding quartic equation having real parts of which some are positive.

A second remark relates to the generality of the form of the differential equations used in the text. Equations such as

$$\frac{d}{dt}\left(\frac{\partial \mathrm{T}}{\partial \dot{x}_r}\right)-\frac{\partial \mathrm{T}}{\partial x_r}+\beta_{r1}\dot{x}_1+\ldots+\beta_{rn}\dot{x}_n+\frac{\partial \mathrm{F}}{\partial \dot{x}_r}+\frac{\partial \mathrm{V}}{\partial x_r}=\mathrm{Q}_r,$$

where β_{rs} is a function of $x_1, \ldots, x_n$ capable of expression in terms of n functions $\beta_1, \ldots, \beta_n$ in the form

$$\beta_{rs}=\frac{\partial \beta_r}{\partial x_s}-\frac{\partial \beta_s}{\partial x_r}$$

are included in this form, with a slight modification due to the presence of the Dissipativity F, and the supposed non-conservative forces Q_r. For this it is only necessary to take

$$\mathrm{L}=\mathrm{T}+\beta_1\dot{x}_1+\ldots+\beta_n\dot{x}_n-\mathrm{V},$$

$$\mathrm{H}=\dot{x}_1\frac{\partial \mathrm{L}}{\partial \dot{x}_1}+\ldots+\dot{x}_n\frac{\partial \mathrm{L}}{\partial \dot{x}_n}-\mathrm{L},$$

and to eliminate $\dot{x}_1, \ldots, \dot{x}_n$, in the familiar way, from the n equations

$$y_r=\frac{\partial \mathrm{L}}{\partial \dot{x}_r}.$$

Then the final equations are

$$\dot{x}_r=\frac{\partial \mathrm{H}}{\partial y_r}, \quad \dot{y}_r=-\frac{\partial \mathrm{H}}{\partial x_r}-\frac{\partial \mathrm{F}}{\partial \dot{x}_r}+\mathrm{Q}_r.$$

Particular illustrations are: (1) the equations of THOMSON and TAIT (as above), p. 392, for which the coefficients β_{rs} are constants. Then we may take $\beta_r = c_{r1}x_1+\ldots+c_{rn}x_n$, where the constant coefficients c_{rs} are in part arbitrary; (2) the equations of Lord KELVIN for liquid motions of ring-shaped solids, 'Collected Papers,' IV. (1910), p. 106; (3) the equations of motion of a system relatively to a rotating frame (LAMB, 'Hydrodynamics,' third edition (1906), p. 294. *Cf.* THOMSON and TAIT, as above, § 319, p. 307, and p. 319), for which we may take, if (ξ, η, ζ) be the co-ordinates of a point of the system relatively to the rotating frame,

$$\beta_r=w\Sigma m\left(\xi\frac{\partial \eta}{\partial x_r}-\eta\frac{\partial \xi}{\partial x_r}\right).$$

The equation of energy in general is at once seen to be

$$\frac{d\mathrm{H}}{dt} = \frac{\partial \mathrm{H}}{\partial t} - \Sigma \dot{x}_r \frac{\partial \mathrm{F}}{\partial \dot{x}_r} + \Sigma \mathrm{Q}_r \dot{x}_r,$$

so that if H be explicitly independent of the time, the forces Q_r be absent, and F be a homogeneous quadratic function of $\dot{x}_1, \ldots, \dot{x}_n$,

$$\frac{d\mathrm{H}}{dt} = -2\mathrm{F}.]$$

§ 17. The simplicity of the formulation depends on the fact that the invariant factors of $\beta^{-1}\alpha - \psi$ are linear. We have obtained this by assuming that the form ap^2 only vanishes when every element of p is zero. But the invariant factors may be linear when this is not so, and the roots of the determinantal equation are not pure imaginaries. For instance, take HILL's equations for the motion of the moon, under certain limitations,

$$\frac{d^2x}{dt^2} - 2n\frac{dy}{dt} + \left(\frac{\mu}{r^3} - 3n^2\right)x = 0, \quad \frac{d^2y}{dt^2} + 2n\frac{dx}{dt} + \frac{\mu y}{r^3} = 0.$$

Writing

$$\mathrm{F} = -\frac{\mu}{r} - \tfrac{3}{2}n^2x^2 + \tfrac{1}{2}(\mathrm{X} + ny)^2 + \tfrac{1}{2}(\mathrm{Y} - nx)^2,$$

these are the same as

$$\frac{dx}{dt} = \frac{\partial \mathrm{F}}{\partial \mathrm{X}}, \quad \frac{d\mathrm{X}}{dt} = -\frac{\partial \mathrm{F}}{\partial x}, \quad \frac{dy}{dt} = \frac{\partial \mathrm{F}}{\partial \mathrm{Y}}, \quad \frac{d\mathrm{Y}}{dt} = -\frac{\partial \mathrm{F}}{\partial y}.$$

The so-called moon of no quadratures is obtained by variation from the solution expressed by

$$x = \sigma, \quad \mathrm{X} = 0, \quad y = 0, \quad \mathrm{Y} = n\sigma,$$

where σ is given by $\mu = 3n^2\sigma^3$; this is a position of relative equilibrium. The matrix ϑ of the notation used above is zero; the matrix a is

$$\begin{pmatrix} -8n^2 & 0 & 0 & -n \\ 0 & 1 & n & 0 \\ 0 & n & 4n^2 & 0 \\ -n & 0 & 0 & 1 \end{pmatrix}.$$

In this case the quadratic form ap^2 is

$$-9n^2p_1^2 + (p_2 + 2np_3)^2 + (np_1 - p_4)^2$$

and vanishes when $p_1 = p_4 = 0$, $p_2 = -2np_3$. But the roots of the determinantal equation

$$|\beta^{-1}\alpha - \psi| = 0$$

are all different, and therefore the invariant factors are linear.

The roots are

$$\psi = \pm\, n\{(28)^{\frac{1}{2}}+1\}^{\frac{1}{2}}, \qquad \psi = \pm\, in\{(28)^{\frac{1}{2}}-1\}^{\frac{1}{2}},$$

of which only two are pure imaginaries; thus not every disturbed orbit is periodic.

§ 18. We pass on now to give the details of the application of the general method above explained to the computation of some particular cases.

A very simple case may be first given, merely as an example of the notation and method, since the results, once obtained, are easily verified.

Take the equations

$$2\frac{dx}{dt} = -x\cos t + y(1+\sin t),$$

$$2\frac{dy}{dt} = -x(1-\sin t) + y\cos t.$$

These may be written

$$\frac{d(x,\, y)}{dt} = \left[\tfrac{1}{2}\begin{pmatrix} 0, & 1 \\ -1, & 0 \end{pmatrix} + \tfrac{1}{2}\begin{pmatrix} -\cos t, & \sin t \\ \sin t, & \cos t \end{pmatrix}\right](x,\, y),$$

or, say,

$$\frac{d(x,\, y)}{dt} = (u+v)(x,\, y),$$

where

$$u = \tfrac{1}{2}\begin{pmatrix} 0, & 1 \\ -1, & 0 \end{pmatrix}, \quad v = \tfrac{1}{2}\begin{pmatrix} -\cos t, & \sin t \\ \sin t, & \cos t \end{pmatrix}.$$

We have at once

$$(2u)^2 = \begin{pmatrix} 0, & 1 \\ -1, & 0 \end{pmatrix}\begin{pmatrix} 0, & 1 \\ -1, & 0 \end{pmatrix} = -1,$$

and therefore

$$\begin{aligned}
\Omega(u) &= 1 + ut + \frac{u^2}{2\,!}t^2 + \frac{u^3}{3\,!}t^3 + \ldots, \\
&= 1 - \frac{1}{2\,!}(\tfrac{1}{2}t)^2 + \frac{1}{4\,!}(\tfrac{1}{2}t)^4 - \ldots + 2u\left\{\tfrac{1}{2}t - \frac{1}{3\,!}(\tfrac{1}{2}t)^3 + \ldots\right\}, \\
&= \cos\tfrac{1}{2}t + \begin{pmatrix} 0, & 1 \\ -1, & 0 \end{pmatrix}\sin\tfrac{1}{2}t, \\
&= \begin{pmatrix} \cos\tfrac{1}{2}t, & \sin\tfrac{1}{2}t \\ -\sin\tfrac{1}{2}t, & \cos\tfrac{1}{2}t \end{pmatrix}.
\end{aligned}$$

This gives

$$\Omega^{-1}(u) = \begin{pmatrix} \cos\tfrac{1}{2}t, & -\sin\tfrac{1}{2}t \\ \sin\tfrac{1}{2}t, & \cos\tfrac{1}{2}t \end{pmatrix}.$$

Wherefore

$$\begin{aligned} \Omega^{-1}(u)\,.\,v\,.\,\Omega(u) &= \tfrac{1}{2}\begin{pmatrix} \cos\tfrac{1}{2}t, & -\sin\tfrac{1}{2}t \\ \sin\tfrac{1}{2}t, & \cos\tfrac{1}{2}t \end{pmatrix}\begin{pmatrix} -\cos t, & \sin t \\ \sin t, & \cos t \end{pmatrix}\Omega(u) \\ &= \tfrac{1}{2}\begin{pmatrix} -\cos\tfrac{1}{2}t, & \sin\tfrac{1}{2}t \\ \sin\tfrac{1}{2}t, & \cos\tfrac{1}{2}t \end{pmatrix}\Omega(u) \\ &= \tfrac{1}{2}\begin{pmatrix} -1, & 0 \\ 0, & 1 \end{pmatrix}. \end{aligned}$$

Denoting this by $\tfrac{1}{2}\sigma$, we find $\sigma^2 = 1$, and hence

$$\begin{aligned} \Omega\left[\Omega^{-1}(u)\,v\,\Omega(u)\right] &= 1+\tfrac{1}{2}\sigma t+\frac{\sigma^2}{2\,!}(\tfrac{1}{2}t)^2+\frac{\sigma^3}{3\,!}(\tfrac{1}{2}t)^3+\ldots, \\ &= ch\tfrac{1}{2}t+\sigma sh\tfrac{1}{2}t, \\ &= \begin{pmatrix} e^{-\frac{1}{2}t}, & 0 \\ 0, & e^{\frac{1}{2}t} \end{pmatrix}. \end{aligned}$$

Thus the solution is

$$(x,\,y) = \Omega(u+v)\,(x^0,\,y^0) = \begin{pmatrix} \cos\tfrac{1}{2}t, & \sin\tfrac{1}{2}t \\ -\sin\tfrac{1}{2}t, & \cos\tfrac{1}{2}t \end{pmatrix}\begin{pmatrix} e^{-\frac{1}{2}t}, & 0 \\ 0, & e^{\frac{1}{2}t} \end{pmatrix}(x^0,\,y^0),$$

namely,

$$\begin{aligned} x &= x^0e^{-\frac{1}{2}t}\cos\tfrac{1}{2}t+y^0e^{\frac{1}{2}t}\sin\tfrac{1}{2}t, \\ y &= -x^0e^{-\frac{1}{2}t}\sin\tfrac{1}{2}t+y^0e^{\frac{1}{2}t}\cos\tfrac{1}{2}t. \end{aligned}$$

The period of the coefficients in the original equation is 2π. The functions $\cos\tfrac{1}{2}t$, $\sin\tfrac{1}{2}t$ have only the period 4π. To bring the result into the form given by the general theory we may write

$$\begin{aligned} x &= x^0e^{-\frac{1}{2}(1+i)t}\,.\,\tfrac{1}{2}(e^{it}+1)+y^0e^{\frac{1}{2}(1+i)t}\,.\,\frac{1}{2i}(1-e^{-it}), \\ y &= -x^0e^{-\frac{1}{2}(1+i)t}\,.\,\frac{1}{2i}(e^{it}-1)+y^0e^{\frac{1}{2}(1+i)t}\,.\,\tfrac{1}{2}(1+e^{-it}), \end{aligned}$$

the so-called characteristic exponents being

$$\pm\tfrac{1}{2}(1+i).$$

§ 19. We now consider cases of the equations

$$\frac{d}{d\tau}(\mathrm{X}, \mathrm{Y}) = -\frac{\psi}{4n}\begin{pmatrix} 1, & -\zeta^{n} \\ \zeta^{-n}, & -1 \end{pmatrix}(\mathrm{X}, \mathrm{Y});$$

these are derivable from the equation

$$\frac{d^2x}{dt^2}+(n^2+\psi)\,x = 0$$

by taking

$$\mathrm{X} = \tfrac{1}{2}e^{int}\left(\frac{dx}{dt}-inx\right), \quad \mathrm{Y} = \tfrac{1}{2}e^{-int}\left(\frac{dx}{dt}+inx\right), \quad \tau = 2it, \quad \zeta = e^{\tau},$$

leading to

$$x = \frac{i}{n}\left(\mathrm{X}e^{-int}-\mathrm{Y}e^{int}\right).$$

As we wish particularly to illustrate the method of obtaining the characteristic exponents from the present point of view, we take first a case in which explicit terms in τ arise early in the method of successive approximation. We take namely $n = 1$, and suppose

$$\frac{\psi}{4} = \lambda h+2\lambda k_1 \cos 2t+2\lambda^2 k_2 \cos 4t+\ldots,$$

$$= \lambda h+\lambda k_1 w_1+\lambda^2 k_2 w_2+\ldots,$$

where λ is small, and w_r is used to denote $\zeta^r+\zeta^{-r}$.

Denoting $\frac{1}{4}\psi$ by ϕ, our differential equations are

$$\frac{d\,(\mathrm{X}, \mathrm{Y})}{d\tau} = u\,(\mathrm{X}, \mathrm{Y}),$$

where

$$u = \begin{pmatrix} -\phi, & \phi\zeta \\ -\phi\zeta^{-1}, & \phi \end{pmatrix}.$$

The coefficients in these equations have period $2\pi i$; by what we have previously shown (§§ 14, 15), the solution is of the form

$$(\mathrm{X}, \mathrm{Y}) = \mathrm{P}h\begin{pmatrix} e^{-q\tau}, & 0 \\ 0, & e^{q\tau} \end{pmatrix}h^{-1}(\mathrm{X}^0, \mathrm{Y}^0),$$

where P is a matrix whose elements have the period $2\pi i$, h is a matrix of constants, and q is the constant which we particularly desire to find. As

$$x = i\left(\mathrm{X}e^{-it}-\mathrm{Y}e^{it}\right),$$

this corresponds to characteristic factors $e^{\mp i(1+2q)t}$ for the original equation in t, whose coefficients have period π. The quantity q is to be found by determining the terms in

τ in the solution of the (X, Y) equations, and forming from this, after putting $\tau = 0$, a determinantal equation (§ 14).

We are to calculate in turn Qu, $QuQu$, &c., and arrange the result according to powers of λ. First we have

$$Qu = \begin{pmatrix} a_1, & b_1 \\ c_1, & d_1 \end{pmatrix},$$

where

$$a_1 = -\int_0^\tau \phi \, d\tau, \qquad b_1 = \int_0^\tau \phi\zeta \, d\tau,$$

$$c_1 = -\int_0^\tau \zeta^{-1}\phi \, d\tau, \quad d_1 = \int_0^\tau \phi \, d\tau \, ;$$

thus, as ϕ is unaltered by changing the sign of τ, b_1 can be obtained from c_1 by changing the sign of τ, and similarly d_1 from a_1. This we denote by writing

$$b_1 = c'_1, \quad d_1 = a'_1.$$

Then

$$uQu = \begin{pmatrix} -\phi, & \zeta\phi \\ -\zeta^{-1}\phi, & \phi \end{pmatrix} \begin{pmatrix} a_1, & c'_1 \\ c_1, & a'_1 \end{pmatrix},$$

$$= \begin{pmatrix} -\phi a_1 + \zeta\phi c_1, & -\phi c'_1 + \zeta\phi a'_1 \\ -\zeta^{-1}\phi a_1 + \phi c_1, & -\zeta^{-1}\phi c'_1 + \phi a'_1 \end{pmatrix},$$

and hence

$$QuQu = \begin{pmatrix} a_2, & c'_2 \\ c_2, & a'_2 \end{pmatrix},$$

where

$$a_2 = \int_0^\tau \phi\,(-a_1 + \zeta c_1)\, d\tau, \qquad c'_2 = \int_0^\tau \phi\,(-c'_1 + \zeta a'_1)\, d\tau,$$

$$c_2 = \int_0^\tau \zeta^{-1}\phi\,(-a_1 + \zeta c_1)\, d\tau, \quad a'_2 = \int_0^\tau \phi\,(a'_1 - \zeta^{-1} c'_1)\, d\tau,$$

so that a'_2 is obtained from a_2 by changing the sign of τ throughout, and similarly c'_2 from c_2. In general, in passing from a term of $\Omega(u)$ involving r integrations to one involving $(r+1)$ integrations, we shall have a law expressible by

$$A_{r+1} = \int_0^\tau \phi\,(-A_r + \zeta C_r)\, d\tau, \quad C_{r+1} = \int_0^\tau \zeta^{-1}\phi\,(-A_r + \zeta C_r)\, d\tau,$$

and the new term, like that from which it is derived, will be of the form

$$\begin{pmatrix} A_{r+1}, & C'_{r+1} \\ C_{r+1}, & A'_{r+1} \end{pmatrix},$$

where A'_{r+1} is derived from A_{r+1} by change of the sign of τ, and similarly C'_{r+1} from C_{r+1}.

Thus, when in $\Omega(u)$ we pick out the coefficient of τ, as it occurs explicitly, independently of its occurrence in ζ, and in this coefficient put $\tau = 0$, we shall obtain a series of the form

$$\begin{pmatrix}\alpha_1, & -\gamma_1\\ \gamma_1, & -\alpha_1\end{pmatrix}+\begin{pmatrix}\alpha_2, & -\gamma_2\\ \gamma_2, & -\alpha_2\end{pmatrix}+\ldots,$$

where the first of these comes from Qu and involves terms in λ and higher powers, the second comes from $QuQu$ and involves terms in λ^2 and higher powers, and so on. And the equation for q will be of the form

$$\begin{vmatrix}\alpha_1+\alpha_2+\ldots-q, & -\gamma_1-\gamma_2-\ldots\\ \gamma_1+\gamma_2+\ldots, & -\alpha_1-\alpha_2-\ldots-q\end{vmatrix} = 0,$$

namely,

$$q^2 = (\alpha_1+\alpha_2+\ldots)^2-(\gamma_1+\gamma_2+\ldots)^2.$$

Further, if the part of Qu which is independent of explicit powers of τ, consisting of elements which are polynomials in ζ, ζ^{-1} and periodic with period $2\pi i$, be denoted by P_1, and similarly the periodic part of $QuQa$ be denoted by P_2, &c., then the periodic matrix P above spoken of will be

$$P = 1+P_1+P_2+\ldots.$$

Proceeding to the computation, retain first only to terms in λ. Then

$$a_1 = -\int_0^\tau \phi\, d\tau = -\lambda h\tau-\lambda k_1(\zeta-\zeta^{-1}),$$

$$c_1 = -\int_0^\tau \zeta^{-1}\phi\, d\tau = -\int_0^\tau \zeta^{-1}[\lambda h+\lambda k_1(\zeta+\zeta^{-1})]\, d\tau,$$

$$= \lambda h(\zeta^{-1}-1)+\lambda k_1\left(\frac{\zeta^{-2}-1}{2}-\tau\right).$$

Hence

$$\alpha_1 = -\lambda h, \quad \gamma_1 = -\lambda k,$$

and q is given by

$$q^2 = \lambda^2(h^2-k_1^2).$$

In the case when the differential equation is that considered by HILL, this gives at once a very near approximation, as he remarks, being equivalent to his formula

$$c^2 = 1+\{(\vartheta_0-1)^2-\vartheta_1^2\}^{\frac{1}{2}}$$

(HILL's 'Collect. Works,' I., p. 260).

If next we retain as far as λ^3, we have from

$$\phi = \lambda h+\lambda k_1(\zeta^{-1}+\zeta)+\lambda^2 k_2(\zeta^{-2}+\zeta^2)+\lambda^3 k_3(\zeta^{-3}+\zeta^3),$$

$$\begin{aligned}-a_1 &= \int_0^\tau \phi\, d\tau \\ &= \lambda h\tau+\lambda k_1(-\zeta^{-1}+\zeta)+\tfrac{1}{2}\lambda^2 k_2(-\zeta^{-2}+\zeta^2)+\tfrac{1}{3}\lambda^3 k_3(-\zeta^{-3}+\zeta^3),\end{aligned}$$

$$\begin{aligned}c_1 &= -\int_0^\tau \zeta^{-1}\phi\, d\tau \\ &= \lambda h(\zeta^{-1}-1)+\lambda k_1\left(\frac{\zeta^{-2}}{2}-\tfrac{1}{2}-\tau\right)+\lambda^2 k_2\left(\frac{\zeta^{-3}}{3}+\tfrac{2}{3}-\zeta\right)+\lambda^3 k_3\left(\frac{\zeta^{-4}}{4}+\tfrac{1}{4}-\frac{\zeta^2}{2}\right)\end{aligned}$$

Hence

$$\begin{aligned}&-a_1+\zeta c_1 \\ &\quad= \lambda h(\tau+1-\zeta)+\lambda k_1\left(-\frac{\zeta^{-1}}{2}+\tfrac{1}{2}\zeta-\tau\zeta\right)+\lambda^2 k_2\left(-\frac{\zeta^{-2}}{6}+\tfrac{2}{3}\zeta-\frac{\zeta^2}{2}\right)+\lambda^3 k_3\left(-\frac{\zeta^{-3}}{12}+\frac{\zeta}{4}-\frac{\zeta^3}{6}\right).\end{aligned}$$

Thus

$$\begin{aligned}&\phi(-a_1+\zeta c_1) \\ &\quad= \lambda^2\{h^2(\tau+1-\zeta)+hk_1(\tau\zeta^{-1}+\tfrac{1}{2}\zeta^{-1}-1+\tfrac{3}{2}\zeta-\zeta^2)+k_1^{\,2}(-\tfrac{1}{2}\zeta^{-2}-\tau-\tau\zeta^2+\tfrac{1}{2}\zeta^2)\} \\ &\qquad +\lambda^3\{hk_2(\tau\zeta^{-2}+\tfrac{5}{6}\zeta^{-2}-\zeta^{-1}+\tfrac{2}{3}\zeta+\tau\zeta^2+\tfrac{1}{2}\zeta^2-\zeta^3) \\ &\qquad\qquad +k_1k_2(-\tfrac{2}{3}\zeta^{-3}-\tau\zeta^{-1}+\tfrac{1}{3}\zeta^{-1}+\tfrac{2}{3}-\zeta+\tfrac{2}{3}\zeta^3-\tau\zeta^3)\}.\end{aligned}$$

This gives

$$\begin{aligned}a_2 &= \int_0^\tau \phi(-a_1+\zeta c_1)\, d\tau \\ &= \lambda^2\{h^2(\tfrac{1}{2}\tau^2+\tau+1-\zeta)+hk_1(-\tau\zeta^{-1}-\tfrac{3}{2}\zeta^{-1}-\tau+\tfrac{1}{2}+\tfrac{3}{2}\zeta-\tfrac{1}{2}\zeta^2) \\ &\qquad +k_1^{\,2}(\tfrac{1}{4}\zeta^{-2}-\tfrac{1}{2}\tau^2-\tfrac{3}{4}-\tfrac{1}{2}\tau\zeta^2+\tfrac{1}{2}\zeta^2)\} \\ &\quad +\lambda^3\{hk_2(-\tfrac{1}{2}\tau\zeta^{-2}-\tfrac{2}{3}\zeta^{-2}+\zeta^{-1}-\tfrac{2}{3}+\tfrac{2}{3}\zeta+\tfrac{1}{2}\tau\zeta^2-\tfrac{1}{3}\zeta^3) \\ &\qquad +k_1k_2(\tfrac{2}{9}\zeta^{-3}+\tau\zeta^{-1}+\tfrac{2}{3}\zeta^{-1}+\tfrac{2}{3}\tau-\tfrac{1}{3}-\zeta+\tfrac{1}{3}\zeta^2-\tfrac{1}{3}\tau\zeta^3+\tfrac{1}{9}\zeta^3)\}.\end{aligned}$$

Similarly,

$$\begin{aligned}c_2 &= \int_0^\tau \zeta^{-1}\phi(-a_1+\zeta c_1)\, d\tau \\ &= \lambda^2\{h^2(-\tau\zeta^{-1}-2\zeta^{-1}-\tau+2)+hk_1(-\tfrac{1}{2}\tau\zeta^{-2}-\tfrac{1}{2}\zeta^{-2}+\zeta^{-1}+\tfrac{3}{2}\tau+\tfrac{1}{2}-\zeta) \\ &\qquad +k_1^{\,2}(\tfrac{1}{6}\zeta^{-3}+\tau\zeta^{-1}+\zeta^{-1}-\tfrac{8}{3}+\tfrac{3}{2}\zeta-\tau\zeta)\} \\ &\quad +\lambda^3\{hk_2(-\tfrac{1}{3}\tau\zeta^{-3}-\tfrac{7}{18}\zeta^{-3}+\tfrac{1}{2}\zeta^{-2}+\tfrac{2}{3}\tau+\tfrac{8}{9}+\tau\zeta-\tfrac{1}{2}\zeta-\tfrac{1}{2}\zeta^2) \\ &\qquad +k_1k_2(\tfrac{1}{6}\zeta^{-4}+\tfrac{1}{2}\tau\zeta^{-2}+\tfrac{1}{12}\zeta^{-2}-\tfrac{2}{3}\zeta^{-1}-\tau-\tfrac{1}{2}+\tfrac{2}{3}\zeta-\tfrac{1}{2}\tau\zeta^2+\tfrac{1}{4}\zeta^2)\}.\end{aligned}$$

Forming now $-a_2+\zeta c_2$ we obtain

$$\begin{aligned}&\lambda^2\{h^2(-\tfrac{1}{2}\tau^2-2\tau-3-\tau\zeta+3\zeta)+hk_1(\tfrac{1}{2}\tau\zeta^{-1}+\zeta^{-1}+\tau+\tfrac{1}{2}+\tfrac{3}{2}\tau\zeta-\zeta-\tfrac{1}{2}\zeta^2) \\ &\qquad +k_1^{\,2}(-\tfrac{1}{12}\zeta^{-2}+\tfrac{1}{2}\tau^2+\tau+\tfrac{7}{4}-\tfrac{8}{3}\zeta+\zeta^2-\tfrac{1}{2}\tau\zeta^2)\} \\ &\quad +\lambda^3\{hk_2(\tfrac{1}{6}\tau\zeta^{-2}+\tfrac{5}{18}\zeta^{-2}-\tfrac{1}{2}\zeta^{-1}+\tfrac{2}{3}+\tfrac{2}{9}\zeta+\tfrac{2}{3}\tau\zeta+\tfrac{1}{2}\tau\zeta^2-\tfrac{1}{2}\zeta^2-\tfrac{1}{6}\zeta^3) \\ &\qquad +k_1k_2(-\tfrac{1}{18}\zeta^{-3}-\tfrac{1}{2}\tau\zeta^{-1}-\tfrac{7}{12}\zeta^{-1}-\tfrac{2}{3}\tau-\tfrac{1}{3}-\tau\zeta+\tfrac{1}{2}\zeta+\tfrac{1}{3}\zeta^2-\tfrac{1}{6}\tau\zeta^3+\tfrac{5}{36}\zeta^3)\}.\end{aligned}$$

To find

$$a_3 = \int_0^\tau \phi\,(-a_2+\zeta c_2)\,d\tau, \qquad c_3 = \int_0^\tau \zeta^{-1}\phi\,(-a_2+\zeta c_2)\,d\tau$$

up to λ^3 it is sufficient to take $\phi = \lambda\,[h+k_1(\zeta^{-1}+\zeta)]$; so we obtain

$$\begin{aligned}
&\phi\,(-a_2+\zeta c_2)\\
&\quad = \lambda^3\,\{h^3\,(-\tfrac{1}{2}\tau^2-2\tau-3-\tau\zeta+3\zeta)\\
&\qquad +h^2k_1\,(-\tfrac{1}{2}\tau^2\zeta^{-1}-\tfrac{3}{2}\tau\zeta^{-1}-2\zeta^{-1}+\tfrac{7}{2}-\tfrac{1}{2}\tau^2\zeta-\tfrac{1}{2}\tau\zeta-4\zeta-\tau\zeta^2+\tfrac{5}{2}\zeta^2)\\
&\qquad +hk_1^2\,(\tfrac{1}{2}\tau\zeta^{-2}+\tfrac{11}{12}\zeta^{-2}+\tau\zeta^{-1}+\tfrac{1}{2}\zeta^{-1}+\tfrac{1}{2}\tau^2+3\tau+\tfrac{7}{4}+\tau\zeta-\tfrac{8}{3}\zeta+\tau\zeta^2-\tfrac{1}{2}\zeta^3)\\
&\qquad +k_1^3(-\tfrac{1}{12}\zeta^{-3}+\tfrac{1}{2}\tau^2\zeta^{-1}+\tau\zeta^{-1}+\tfrac{5}{3}\zeta^{-1}-\tfrac{8}{3}+\tfrac{1}{2}\tau^2\zeta+\tfrac{1}{2}\tau\zeta+\tfrac{11}{4}\zeta-\tfrac{8}{3}\zeta^2-\tfrac{1}{2}\tau\zeta^3+\zeta^3)\},
\end{aligned}$$

and hence

$$\begin{aligned}
a_3 &= \int_0^\tau \phi\,(-a_2+\zeta c_2)\,d\tau\\
&= \lambda^3h^3\,(-\tfrac{1}{6}\tau^3-\tau^2-3\tau-4-\tau\zeta+4\zeta)\\
&\quad +\lambda^3h^2k_1\,[(\tfrac{1}{2}\tau^2+\tfrac{5}{2}\tau+\tfrac{9}{2})\,\zeta^{-1}+\tfrac{7}{2}\tau-\tfrac{3}{2}+(-\tfrac{1}{2}\tau^2+\tfrac{1}{2}\tau-\tfrac{9}{2})\,\zeta+(-\tfrac{1}{2}\tau+\tfrac{3}{2})\,\zeta^2]\\
&\quad +\lambda^3hk_1^2\Big[(-\tfrac{1}{4}\tau-\tfrac{7}{12})\,\zeta^{-2}+(-\tau-\tfrac{3}{2})\,\zeta^{-1}+\tfrac{1}{36}\tau^3+\tfrac{3}{2}\tau^2+\tfrac{7}{4}\tau+\tfrac{37}{6}+(\tau-\tfrac{11}{3})\,\zeta\\
&\qquad\qquad +\left(\frac{\tau}{2}-\tfrac{1}{4}\right)\zeta^2-\tfrac{1}{6}\zeta^3\Big],\\
&\quad +\lambda^3k_1^3\,[\tfrac{1}{36}\zeta^{-3}+(-\tfrac{1}{2}\tau^2-2\tau-\tfrac{11}{3})\,\zeta^{-1}-\tfrac{8}{3}\tau+\tfrac{4}{3}+(\tfrac{1}{2}\tau^2-\tfrac{1}{2}\tau+\tfrac{13}{4})\,\zeta-\tfrac{4}{3}\zeta^2+(-\tfrac{1}{6}\tau+\tfrac{7}{18})\,\zeta^3].
\end{aligned}$$

Similarly,

$$\begin{aligned}
c_3 &= \int_0^\tau \zeta^{-1}\phi\,(-a_2+\zeta c_2)\,d\tau\\
&= \lambda^3h^3\,[(\tfrac{1}{2}\tau^2+3\tau+6)\,\zeta^{-1}+(-\tfrac{1}{2}\tau^2+3\tau-6)]\\
&\quad +\lambda^3h^2k_1\,[(\tfrac{1}{4}\tau^2+\tau+\tfrac{3}{2})\,\zeta^{-2}-\tfrac{7}{2}\zeta^{-1}+(-\tfrac{1}{6}\tau^3-\tfrac{1}{4}\tau^2-4\tau-\tfrac{3}{2})+(-\tau+\tfrac{7}{2})\,\zeta]\\
&\quad +\lambda^3hk_1^2\,[(-\tfrac{1}{6}\tau-\tfrac{13}{36})\,\zeta^{-3}-\tfrac{1}{2}\,(\tau+1)\,\zeta^{-2}+(-\tfrac{1}{2}\tau^2-4\tau-\tfrac{23}{4})\,\zeta^{-1}\\
&\qquad\qquad +\tfrac{1}{2}\tau^2-\tfrac{8}{3}\tau+\tfrac{283}{36}+\tau\zeta-\zeta-\tfrac{1}{4}\zeta^2]\\
&\quad +\lambda^3k_1^3\,[\tfrac{1}{48}\zeta^{-4}+(-\tfrac{1}{4}\tau^2-\tfrac{3}{4}\tau-\tfrac{29}{24})\,\zeta^{-2}+\tfrac{8}{3}\zeta^{-1}+\tfrac{1}{6}\tau^3+\tfrac{1}{4}\tau^2+\tfrac{11}{4}\tau+\tfrac{9}{16}-\tfrac{8}{3}\zeta+(-\tfrac{1}{4}\tau+\tfrac{5}{8})\,\zeta^2].
\end{aligned}$$

Picking out now the terms in τ, putting therein $\zeta = 1$, and using the notation previously explained, we have, up to λ^3,

$$\begin{aligned}
\alpha_1 &= -\lambda h, & \gamma_1 &= -\lambda k_1,\\
\alpha_2 &= \lambda^2\,(h^2-2hk_1-\tfrac{1}{2}k_1^2)+\lambda^3\,(\tfrac{4}{3}k_1k_2), & \gamma_2 &= \lambda^2\,(-2h^2+hk_1)+\lambda^3\,(\tfrac{4}{3}hk_2-k_1k_2),\\
\alpha_3 &= \lambda^3\,(-4h^3+6h^2k_1+2hk_1^2-\tfrac{16}{3}k_1^3), & \gamma_3 &= \lambda^3\,(6h^3-4h^2k_1-\tfrac{19}{3}hk_1^2+\tfrac{7}{4}k_1^3).
\end{aligned}$$

Hence

$$-(\alpha_1+\alpha_2+\alpha_3+\gamma_1+\gamma_2+\gamma_3)$$
$$= \lambda(h+k_1)+\lambda^2(h^2+hk_1+\tfrac{1}{2}k_1^2)+\lambda^3(-2h^3-2h^2k_1+\tfrac{13}{3}hk_1^2+\tfrac{43}{12}k_1^3-\tfrac{4}{3}hk_2-\tfrac{1}{3}k_1k_2)$$

and

$$-(\alpha_1+\alpha_2+\alpha_3)+\gamma_1+\gamma_2+\gamma_3$$
$$= \lambda(h-k_1)+\lambda^2(-3h^2+3hk_1+\tfrac{1}{2}k_1^2)+\lambda^3(10h^3-10h^2k_1-\tfrac{25}{3}hk_1^2+\tfrac{4}{3}hk_2+\tfrac{85}{12}k_1^3-\tfrac{7}{3}k_1k_2).$$

The product of these gives the value of q^2, namely,

$$q^2 = \lambda^2(h^2-k_1^2)-\lambda^3 h(2h^2-3k_1^2)+\lambda^4[5(h^2-k_1^2)^2-\tfrac{5}{4}k_1^4-2k_1^2k_2].$$

This agrees with the value found above by a quite different method (§ 4).

The matrix of coefficients of τ, after ζ has been replaced by 1, is of the form

$$A_0 = \begin{pmatrix} \alpha, & -\gamma \\ \gamma, & -\alpha \end{pmatrix},$$

and its square is $(\alpha^2-\gamma^2)$ times the matrix unity. The matrix $\Omega_0^w(u)$ of § 14 is thus

$$\Omega_0^w(u) = 1+A_0w+\tfrac{1}{2}q^2w^2+\frac{1}{3!}q^2A_0w^3+\frac{1}{4!}q^4w^4+\ldots$$

or

$$\begin{pmatrix} C+\alpha S, & -\gamma S \\ \gamma S, & C-\alpha S \end{pmatrix},$$

where $C = ch(qw)$, $S = \dfrac{1}{q}sh(qw)$. From this it is easily seen that for the calculation of q the method we have followed is less laborious than to use the equation

$$|\Omega_0^w(u)-\rho| = 0.$$

The differential equation from which we have started is, to terms in k_2, if we suppose $\lambda = 1$,

$$\frac{d^2x}{dt^2}+(1+4h+8k_1\cos 2t+8k_2\cos 4t)x = 0.$$

If we compare this with the form considered by HILL (' Coll. Works,' I., pp. 246, 268), we have, with his numerical values,

$$h = 0{\cdot}03971\ 09848\ 99146,$$
$$k_1 = -0{\cdot}01426\ 10046\ 86726,$$
$$k_2 = 0{\cdot}00009\ 58094\ 99389.$$

§ 20. Consider now briefly the case of the equations

$$\frac{d}{d\tau}(\mathrm{X}, \mathrm{Y}) = \frac{\psi}{4n}\begin{pmatrix} -1, & \zeta^{n} \\ -\zeta^{-n}, & 1 \end{pmatrix}(\mathrm{X}, \mathrm{Y}),$$

in which $n = 2$. We suppose

$$\frac{\psi}{4n} = \lambda h + \lambda k_1 w_1 + \lambda^2 k_2 w_2 + \ldots, \quad = \phi, \text{ say},$$

$$w_r = \zeta^{-r} + \zeta^{r},$$

$$u = \begin{pmatrix} -\phi, & \zeta^{n}\phi \\ -\zeta^{-n}\phi, & \phi \end{pmatrix}.$$

As in the case of $n = 1$,

$$\mathrm{Q}u = \begin{pmatrix} a_1, & c'_1 \\ c_1, & a'_1 \end{pmatrix},$$

where

$$a_1 = -\int_0^{\tau} \phi \, d\tau = -\lambda h \tau + \lambda k_1 (\zeta^{-1} - \zeta) + \tfrac{1}{2}\lambda^2 k_2 (\zeta^{-2} - \zeta^{2}),$$

and, for $n = 2$,

$$c_1 = -\int_0^{\tau} \zeta^{-2}\phi \, d\tau = \lambda h (\tfrac{1}{2}\zeta^{-2} - \tfrac{1}{2}) + \lambda k_1 (\tfrac{1}{3}\zeta^{-3} + \zeta^{-1} - \tfrac{4}{3}) + \lambda^2 k_2 (\tfrac{1}{4}\zeta^{-4} - \tfrac{1}{4} - \tau).$$

These give

$$\begin{aligned} &\phi(-a_1 + \zeta^2 c_1) \\ &\quad = \lambda^2 h^2 (\tau + \tfrac{1}{2} - \tfrac{1}{2}\zeta^2) + \lambda^2 h k_1 \left[(\tau - \tfrac{1}{6})\zeta^{-1} + (\tau + 2)\zeta - \tfrac{4}{3}\zeta^2 - \tfrac{1}{2}\zeta^3\right] \\ &\qquad + \lambda^2 k_1{}^2 (-\tfrac{2}{3}\zeta^{-2} + \tfrac{4}{3} - \tfrac{4}{3}\zeta + 2\zeta^2 - \tfrac{4}{3}\zeta^3). \end{aligned}$$

As before

$$\mathrm{Q}u\mathrm{Q}u = \begin{pmatrix} a_2, & c'_2 \\ c_2, & a'_2 \end{pmatrix},$$

where

$$\begin{aligned} a_2 &= \int_0^{\tau} \phi(-a_1 + \zeta^2 c_1) \, d\tau \\ &= \lambda^2 h^2 (\tfrac{1}{2}\tau^2 + \tfrac{1}{2}\tau - \tfrac{1}{4}\zeta^2 + \tfrac{1}{4}) + \lambda^2 h k_1 (-\tau\zeta^{-1} - \tfrac{5}{6}\zeta^{-1} + \tfrac{2}{3} + \tau\zeta + \zeta - \tfrac{2}{3}\zeta^2 - \tfrac{1}{6}\zeta^3) \\ &\qquad + \lambda^2 k_1{}^2 (\tfrac{1}{3}\zeta^{-2} + \tfrac{4}{3}\tau + \tfrac{4}{9} - \tfrac{4}{3}\zeta + \zeta^2 - \tfrac{4}{9}\zeta^3) \end{aligned}$$

and

$$c_2 = \int_0^\tau \zeta^{-2}\phi\,(-a_1+\zeta^2 c_1)\,d\tau$$

$$= \lambda^2 h^2\left(-\tfrac{1}{2}\tau\zeta^{-2}-\tfrac{1}{2}\zeta^{-2}+\tfrac{1}{2}-\frac{\tau}{2}\right)+\lambda^2 hk_1\left(-\tfrac{1}{3}\tau\zeta^{-3}-\tfrac{1}{18}\zeta^{-3}-\tau\zeta^{-1}-3\zeta^{-1}+\tfrac{32}{9}-\tfrac{4}{3}\tau-\tfrac{1}{2}\zeta\right)$$

$$+\lambda^2 k_1^{\,2}\left(\tfrac{1}{6}\zeta^{-4}-\tfrac{2}{3}\zeta^{-2}+\tfrac{4}{3}\zeta^{-1}+2\tau+\tfrac{1}{2}-\tfrac{4}{3}\zeta\right).$$

Picking out the coefficients of τ in these, and putting therein $\zeta = 1$, we have

$$\alpha_1 = -\lambda h, \qquad \gamma_1 = -\lambda^2 k_2,$$

$$\alpha_2 = \tfrac{1}{2}\lambda^2 h^2+\tfrac{4}{3}\lambda^2 k_1^{\,2}, \quad \gamma_2 = -\lambda^2 h^2-\tfrac{8}{3}\lambda^2 hk_1+2\lambda^2 k_1^{\,2},$$

and hence, to λ^3,

$$q^2 = (\alpha_1+\alpha_2)^2-(\gamma_1+\gamma_2)^2 = \left[\lambda h-\frac{\lambda^2}{2}(h^2+\tfrac{8}{3}k_1^{\,2})\right]^2-[\lambda^2(\quad)]^2,$$

$$= \lambda^2 h^2-\lambda^3 h\,(h^2+\tfrac{8}{3}k_1^{\,2}).$$

This agrees with a result previously found (§ 6), but fails to give the first term in q^2 if $h = 0$. When this is so it is necessary to take account of the terms in λ^3. By taking terms in λ^3 in a_1, c_1, we only obtain terms in $\phi\,(-a_1+\zeta^2 c_1)$ which involve λ^4. But the terms in λ^2 in a_1, c_1 which are written down give terms in λ^3 in $\phi\,(-a_1+\zeta^2 c_1)$, which are

$$\lambda^2 hk_2\left(\tfrac{1}{4}\zeta^{-2}+\tau\zeta^{-2}-\tfrac{1}{2}+\tfrac{3}{4}\zeta^2-\tfrac{1}{2}\zeta^4\right)+\lambda^3 k_1 k_2\left(-\tfrac{11}{12}\zeta^{-3}+\tfrac{7}{4}\zeta^{-1}-\tfrac{4}{3}-\tfrac{5}{12}\zeta-\tau\zeta+\tfrac{9}{4}\zeta^3-\tau\zeta^3-\tfrac{4}{3}\zeta^4\right),$$

and hence the additional terms in a_2

$$\lambda^3 hk_2\left(-\tfrac{1}{2}\tau\zeta^{-2}-\tfrac{3}{8}\zeta^{-2}-\tfrac{1}{2}\tau+\tfrac{1}{8}+\tfrac{3}{8}\zeta^2-\tfrac{1}{8}\zeta^4\right)$$

$$+\lambda^3 k_1 k_2\left(\tfrac{11}{36}\zeta^{-3}-\tfrac{7}{4}\zeta^{-1}-\tfrac{4}{3}\tau+\tfrac{7}{12}\zeta-\tau\zeta+\tfrac{31}{36}\zeta^3-\tfrac{1}{3}\tau\zeta^3-\tfrac{1}{3}\zeta^4+\tfrac{1}{3}\right),$$

and the additional terms in c_2

$$\lambda^3 hk_2\left(-\tfrac{1}{4}\tau\zeta^{-4}-\tfrac{1}{8}\zeta^{-4}+\tfrac{1}{4}\zeta^{-2}+\tfrac{3}{4}\tau+\tfrac{1}{8}-\frac{\zeta^2}{4}\right)$$

$$+\lambda^3 k_1 k_2\left(\tfrac{11}{60}\zeta^{-5}-\tfrac{7}{12}\zeta^{-3}+\tfrac{2}{3}\zeta^{-2}+\tfrac{17}{12}\zeta^{-1}+\tau\zeta^{-1}+\tfrac{13}{4}\zeta-\tau\zeta-\tfrac{2}{3}\zeta^2-\tfrac{64}{15}\right).$$

In finding the terms in λ^3 in a_3, c_3, it is sufficient to retain the terms λ^2 in a_2 and c_2. This gives for $\phi\,(-a_2+\zeta^2 c_2)$,

$$\lambda^3 h^3\left\{-\tfrac{1}{2}\tau^2-\tau-\tfrac{3}{4}+\tfrac{3}{4}\zeta^2-\tfrac{1}{2}\tau\zeta^2\right\}$$

$$+\lambda^3 h^2 k_1\left\{\zeta^{-1}\left(-\tfrac{1}{2}\tau^2-\tfrac{1}{3}\tau+\tfrac{1}{36}\right)-\tfrac{2}{3}+\zeta\left(-\tfrac{1}{2}\tau^2-\tfrac{7}{2}\tau-4\right)+\zeta^2\left(-\tfrac{4}{3}\tau+\tfrac{38}{9}\right)+\zeta^3\left(-\tfrac{1}{2}\tau+\tfrac{5}{12}\right)\right\}$$

$$+\lambda^3 hk_1^{\,2}\left\{\zeta^{-2}\left(\tfrac{2}{3}\tau+\tfrac{11}{18}\right)-\tfrac{2}{3}\zeta^{-1}-\tfrac{8}{3}\tau-\tfrac{13}{3}+\zeta\left(-\tfrac{4}{3}\tau+\tfrac{56}{9}\right)-\tfrac{29}{6}\zeta^2+\zeta^3\left(-\tfrac{4}{3}\tau+\tfrac{10}{3}\right)-\tfrac{1}{3}\zeta^4\right\}$$

$$+\lambda^3 k_1^{\,3}\left\{-\tfrac{1}{6}\zeta^{-3}-\zeta^{-1}\left(\tfrac{4}{3}\tau+\tfrac{23}{18}\right)+\tfrac{8}{3}+\zeta\left(\tfrac{2}{3}\tau-\tfrac{29}{18}\right)+\tfrac{16}{9}\zeta^2+\zeta^3\left(2\tau-\tfrac{1}{2}\right)-\tfrac{8}{9}\zeta^4\right\}.$$

For $a_3 = \int_0^\tau \phi\,(-a_2+\zeta^2 c_2)\,d\tau$, this leads to

$$\begin{aligned}
&\lambda^3 h^3\,\{-\tfrac{1}{6}\tau^3-\tfrac{1}{2}\tau^2-\tfrac{3}{4}\tau-\tfrac{1}{2}+\zeta^2\,(-\tfrac{1}{4}\tau+\tfrac{1}{2})\}\\
&\quad+\lambda^3 h^2 k_1\left\{\zeta^{-1}\,(\tfrac{1}{2}\tau^2+\tfrac{4}{3}\tau+\tfrac{47}{36})-\tfrac{2}{3}\tau-\tfrac{22}{9}+\zeta\,(-\tfrac{1}{2}\tau^2-\tfrac{5}{2}\tau-\tfrac{3}{2})\right.\\
&\qquad\qquad\left.+\zeta^2\,(-\tfrac{2}{3}\tau+\tfrac{22}{9})+\zeta^3\left(-\frac{\tau}{6}+\tfrac{7}{36}\right)\right\}\\
&\quad+\lambda^3 h k_1^{\,2}\,\{-\zeta^{-2}\,(\tfrac{1}{3}\tau+\tfrac{17}{36})+\tfrac{2}{3}\zeta^{-1}-\tfrac{4}{3}\tau^2-\tfrac{13}{3}\tau-\tfrac{703}{108}+\zeta\,(-\tfrac{4}{3}\tau+\tfrac{68}{9})\\
&\qquad\qquad-\tfrac{29}{12}\zeta^2+\zeta^3\,(-\tfrac{4}{9}\tau+\tfrac{34}{27})-\tfrac{1}{12}\zeta^4\}\\
&\quad+\lambda^3 k_1^{\,3}\,\{\tfrac{1}{18}\zeta^{-3}+\zeta^{-1}\,(\tfrac{4}{3}\tau+\tfrac{47}{18})+\tfrac{8}{3}\tau-\tfrac{2}{3}+\zeta\,(\tfrac{2}{3}\tau-\tfrac{41}{18})+\tfrac{8}{9}\zeta^2+\zeta^3\,(\tfrac{2}{3}\tau-\tfrac{7}{18})-\tfrac{2}{9}\zeta^4\}.
\end{aligned}$$

The terms in $c_3 = \int_0^\tau \zeta^{-2}\phi\,(-a_2+\zeta^2 c_2)\,d\tau$ are similarly

$$\begin{aligned}
&\lambda^3 h^3\,\{\zeta^{-2}\,(\tfrac{1}{4}\tau^2+\tfrac{1}{4}\tau)+\tfrac{3}{4}\tau-\tfrac{1}{4}\tau^2\}\\
&\quad+\lambda^3 h^2 k_1\left\{\zeta^{-3}\left(\tfrac{1}{6}\tau^2+\frac{2\tau}{9}+\tfrac{7}{108}\right)+\tfrac{1}{3}\zeta^{-2}+\zeta^{-1}\,(\tfrac{1}{2}\tau^2+\tfrac{9}{2}\tau+\tfrac{17}{2})\right.\\
&\qquad\qquad\left.-\tfrac{265}{27}-\tfrac{2}{3}\tau^2+\tfrac{38}{9}\tau+\zeta\,(-\tfrac{1}{2}\tau+\tfrac{11}{12})\right\}\\
&\quad+\lambda^3 h k_1^{\,2}\left\{\zeta^{-4}\left(-\frac{\tau}{6}-\tfrac{7}{36}\right)+\tfrac{2}{9}\zeta^{-3}+\zeta^{-2}\,(\tfrac{4}{3}\tau+\tfrac{17}{6})+\zeta^{-1}\,(\tfrac{4}{3}\tau-\tfrac{44}{9})\right.\\
&\qquad\qquad\left.-\tfrac{89}{36}-\tfrac{29}{6}\tau+\zeta\,(-\tfrac{4}{3}\tau+\tfrac{14}{3})-\tfrac{1}{6}\zeta^2\right\}\\
&\quad+\lambda^3 k_1^{\,3}\,\{\tfrac{1}{30}\zeta^{-5}+\zeta^{-3}\,(\tfrac{4}{9}\tau+\tfrac{31}{54})-\tfrac{4}{3}\zeta^{-2}+\zeta^{-1}\,(-\tfrac{2}{3}\tau+\tfrac{17}{18})\\
&\qquad\qquad+\tfrac{368}{135}+\tfrac{16}{9}\tau+\zeta\,(2\tau-\tfrac{5}{2})-\tfrac{4}{9}\zeta^2\}.
\end{aligned}$$

It is easy to see that the terms in λ^3 in a_1, c_1 are respectively

$$\tfrac{1}{3}\lambda^3 k_3\,(\zeta^{-3}-\zeta^3) \quad\text{and}\quad \lambda^3 k_3\,(\tfrac{1}{5}\zeta^{-5}-\zeta+\tfrac{4}{5}),$$

neither of which contains τ. Thus up to λ^3 we have, in the preceding notation

$$\begin{aligned}
\alpha_1 &= -\lambda h, & \gamma_1 &= -\lambda^2 k_2,\\
\alpha_2 &= \tfrac{1}{2}\lambda^2\,(h^2+\tfrac{8}{3}k_1^{\,2})-\lambda^3\,(hk_2+\tfrac{8}{3}k_1k_2), & \gamma_2 &= -\lambda^2\,(h^2+\tfrac{8}{3}hk_1-2k_1^{\,2})+\tfrac{1}{2}\lambda^3 hk_2,\\
\alpha_3 &= -\lambda^3 h^3-\tfrac{8}{3}\lambda^3 h^2 k_1-\tfrac{58}{9}\lambda^3 hk_1^{\,2}+\tfrac{16}{3}\lambda^3 k_1^{\,3}, & \gamma_3 &= \lambda^3 h^3+\tfrac{76}{9}\lambda^3 h^2 k_1-\tfrac{11}{3}\lambda^3 hk_1^{\,2}+\tfrac{32}{9}\lambda^3 k_1^{\,3}.
\end{aligned}$$

Thus

$$\begin{aligned}
\alpha_1+\alpha_2+\alpha_3 &= -\lambda h+\tfrac{1}{2}\lambda^2\,(h^2+\tfrac{8}{3}k_1^{\,2})+\lambda^3\,(-h^3-\tfrac{8}{3}h^2k_1-\tfrac{58}{9}hk_1^{\,2}+\tfrac{16}{3}k_1^{\,3}-hk_2-\tfrac{8}{3}k_1k_2),\\
\gamma_1+\gamma_2+\gamma_3 &= \lambda^2\,(-h^2-\tfrac{8}{3}hk_1+2k_1^{\,2}-k_2)+\lambda^3\,(h^3+\tfrac{76}{9}h^2k_1-\tfrac{11}{3}hk_1^{\,2}+\tfrac{32}{9}k_1^{\,3}+\tfrac{1}{2}hk_2).
\end{aligned}$$

This gives

$$q^2 = (\alpha_1+\alpha_2+\alpha_3)^2-(\gamma_1+\gamma_2+\gamma_3)^2$$
$$= \lambda^2h^2-\lambda^3h\,(h^2+\tfrac{8}{3}k_1^{\,2})+\lambda^4\,(\tfrac{5}{4}h^4+\tfrac{100}{9}h^2k_1^{\,2}-\tfrac{20}{9}k_1^{\,4}-k_2^{\,2}+4k_1^{\,2}k_2)$$

as far as terms in λ^4. This result is for the equation

$$\frac{d^2x}{dt^2}+(n^2+\psi)\,x = 0,$$

wherein $n = 2$ and

$$\frac{\psi}{8} = \lambda h+\lambda k_1\,(\zeta^{-1}+\zeta)+\lambda^2k_2\,(\zeta^{-2}+\zeta^2)+\ldots$$

and agrees with the result previously found (§ 6) when in this last we replace h, k_1, k_2 respectively by $2h$, $2k_1$, $2k_2$, as is necessary, taking account of the difference of notation for $\frac{\psi}{4}$ in the two cases. By an independent investigation for the case when

$$\frac{\psi}{8} = \lambda h_1+\lambda k_1\,(\zeta^{-1}+\zeta)+\lambda^2h_2+\lambda^2k_2\,(\zeta^{-2}+\zeta^2)+\lambda^3h_3+\lambda^3k_3\,(\zeta^{-3}+\zeta^3)+\ldots$$

we have found (above, p. 142),

$$q^2 = h_1^{\,2}\lambda^2-h_1\,(h_1^{\,2}+\tfrac{8}{3}k_1^{\,2}-2h_2)\,\lambda^3$$
$$+\lambda^4\,\{(\tfrac{1}{2}h_1^{\,2}+\tfrac{4}{3}k_1^{\,2}-h_2)^2+h_1^{\,4}+\tfrac{88}{9}h_1^{\,2}k_1^{\,2}-2h_1^{\,2}h_2+2h_1h_3-(k_2-2k_1^{\,2})^2\}+\ldots,$$

which, replacing h by $h_1+h_2\lambda+h_3\lambda^2$, arises from the preceding result.

§ 21. Now consider the equations

$$\frac{d}{d\tau}(\mathrm{X},\,\mathrm{Y}) = u\,(\mathrm{X},\,\mathrm{Y}),$$

where

$$u = \begin{pmatrix} -\phi, & \zeta^n\phi \\ -\zeta^{-n}\phi, & \phi \end{pmatrix}$$

and n is not 1 or 2, but is an integer if u is a periodic matrix.

With

$$\phi = \lambda h+\lambda k_1\,(\zeta^{-1}+\zeta)+\lambda^2k_2\,(\zeta^{-2}+\zeta^2)+\ldots$$

we have, retaining only to λ^2,

$$a_1 = -\int_0^\tau \phi\,d\tau = -\lambda h\tau+\lambda k_1\,(\zeta^{-1}-\zeta)+\tfrac{1}{2}\lambda^2k_2\,(\zeta^{-2}-\zeta^2),$$

$$c_1 = -\int_0^\tau \zeta^{-n}\phi\,d\tau = -\int_0^\tau [\lambda h\zeta^{-n}+\lambda k_1\,(\zeta^{-n-1}+\zeta^{-n+1})+\lambda^2k_2\,(\zeta^{-n-2}+\zeta^{-n+2})]\,d\tau$$
$$= \frac{1}{n}\lambda h\,(\zeta^{-n}-1)+\lambda k_1\left(\frac{\zeta^{-n-1}}{n+1}+\frac{\zeta^{-n+1}}{n-1}-\frac{2n}{n^2-1}\right)+\lambda^2k_2\left(\frac{\zeta^{-n-2}}{n+2}+\frac{\zeta^{-n+2}}{n-2}-\frac{2n}{n^2-4}\right),$$

which lead to

$$\begin{aligned}\phi(-a_1+\zeta^n c_1) = {} & \lambda^2h^2\left(\tau+\frac{1-\zeta^n}{n}\right) \\ & +\lambda^2hk_1\left\{\zeta^{-1}\left(\tau-\frac{n^2-n-1}{n(n+1)}\right)+\zeta\left(\tau+\frac{n^2+n-1}{n(n-1)}\right)-\frac{\zeta^{n-1}}{n}-\frac{2n}{n^2-1}\zeta^n-\frac{\zeta^{n+1}}{n}\right\} \\ & +\lambda^2k_1^{\,2}\left\{-\frac{n}{n+1}\zeta^{-2}+\frac{2n}{n^2-1}+\frac{n}{n-1}\zeta^2-\frac{2n}{n^2-1}\zeta^{n-1}-\frac{2n}{n^2-1}\zeta^{n+1}\right\},\end{aligned}$$

so that

$$\begin{aligned}a_2 &= \int_0^\tau \phi(-a_1+\zeta^n c_1)\,d\tau \\ &= \lambda^2h^2\left(\tfrac{1}{2}\tau^2+\frac{\tau}{n}-\frac{\zeta^n-1}{n^2}\right) \\ &\quad +\lambda^2hk_1\left\{-\zeta^{-1}\left(\tau+\frac{2n+1}{n(n+1)}\right)+\zeta\left(\tau+\frac{2n-1}{n(n-1)}\right)\right. \\ &\qquad\qquad \left.+\frac{4}{n^2-1}-\frac{\zeta^{n-1}}{n(n-1)}-\frac{2}{n^2-1}\zeta^n-\frac{\zeta^{n+1}}{n(n+1)}\right\} \\ &\quad +\lambda^2k_1^{\,2}\left\{\frac{n}{2(n+1)}\zeta^{-2}+\frac{2n}{n^2-1}\tau-\frac{n^2(n^2-5)}{(n^2-1)^2}\right. \\ &\qquad\qquad \left.+\frac{n}{2(n-1)}\zeta^2-\frac{2n}{(n-1)(n^2-1)}\zeta^{n-1}-\frac{2n}{(n+1)(n^2-1)}\zeta^{n+1}\right\}.\end{aligned}$$

Similarly,

$$\begin{aligned}c_2 &= \int_0^\tau \zeta^{-n}\phi(-a_1+\zeta^n c_1)\,d\tau \\ &= \lambda^2h^2\left(-\frac{\tau\zeta^{-n}}{n}-\frac{2\zeta^{-n}}{n^2}+\frac{2}{n^2}-\frac{\tau}{n}\right) \\ &\quad +\lambda^2hk_1\left\{-\frac{\zeta^{-n-1}}{n+1}\left(\tau-\frac{n^2-2n-1}{n(n+1)}\right)-\frac{\zeta^{-n+1}}{n-1}\left(\tau+\frac{n^2+2n-1}{n(n-1)}\right)\right. \\ &\qquad\qquad \left.+\frac{\zeta^{-1}}{n}-\frac{2n\tau}{n^2-1}-\frac{\zeta}{n}+\frac{8n^2}{(n^2-1)^2}\right\} \\ &\quad +\lambda^2k_1^{\,2}\left\{\frac{n}{(n+1)(n+2)}\zeta^{-n-2}-\frac{2}{n^2-1}\zeta^{-n}-\frac{n}{(n-1)(n-2)}\zeta^{-n+2}\right. \\ &\qquad\qquad \left.+\frac{2n}{n^2-1}\zeta^{-1}-\frac{2n}{n^2-1}\zeta+\frac{8}{n^2-4}\right\}.\end{aligned}$$

Thus we have, so far as terms in λ^2,

$$\alpha_1 = -\lambda h, \qquad \gamma_1 = 0,$$

$$\alpha_2 = \frac{\lambda^2h^2}{n}+\lambda^2k_1^{\,2}\frac{2n}{n^2-1}, \quad \gamma_2 = -\frac{2\lambda^2h^2}{n}-\frac{4\lambda^2hk_1n}{n^2-1},$$

and so, to this approximation,

$$\pm q = \alpha_1 + \alpha_2 = -\lambda h + \frac{\lambda^2 h^2}{n} + \lambda^2 k_1^2 \,.\, \frac{2n}{n^2-1}\,.$$

The characteristic factor is then $e^{i(n+2q)t}$, the differential equation being

$$\frac{d^2x}{dt^2} + (n^2 + 4n\lambda h + 8n\lambda k_1 \cos 2t + 8n\lambda^2 k_2 \cos 4t + \ldots)\, x = 0.$$

Thus q is always real, when λ is small enough, provided k_1 is not zero, even if h be zero. The result agrees with that found in § 6 for $n = 3$, if allowance be made for the change of notation.

[*December 1, 1915.*—Consider the differential equation differing from that just preceding only by the substitution of H for λh in the term $4n\lambda h$ of the coefficient of x, where H is supposed to be of the form $\lambda h_1 + \lambda^2 h_2 + \lambda^3 h_3 + \ldots$. The computation of q^2 proceeds then exactly as before. The formulæ for $\alpha_1 + \alpha_2 + \alpha_3$, $\gamma_1 + \gamma_2 + \gamma_3$, given above, p. 178, substituting H for λh, show that, for $n = 1$, q^2 is then of the form $(\mathrm{H} - \alpha_1)(\mathrm{H} - \alpha_2)\,\mathrm{Q}$, wherein Q is a power series in H, λk_1, $\lambda^2 k_2$, …, reducing to 1 when $\mathrm{H} = 0$, $\lambda = 0$, and

$$\alpha_1 = -k_1\lambda - \tfrac{1}{2}k_1^2\lambda^2 + (\tfrac{1}{4}k_1^3 - k_1k_2)\,\lambda^3 + \ldots,$$

$$\alpha_2 = k_1\lambda - \tfrac{1}{2}k_1^2\lambda^2 - (\tfrac{1}{4}k_1^3 - k_1k_2)\,\lambda^3 + \ldots.$$

The value of q^2 is positive, and the motion represented by the differential equation is stable, so long as H does not lie between these values. Similarly for $n = 2$, from the formulæ at the bottom of p. 181, the range in which q^2 is negative is when H lies between

$$-(\tfrac{2}{3}k_1^2 - k_2)\,\lambda^2 \quad \text{and} \quad (\tfrac{10}{3}k_1^2 - k_2)\,\lambda^2,$$

these being accurate as far as λ^3. Unless $\tfrac{2}{3}k_1^2 < k_2 < \tfrac{10}{3}k_1^2$, these limits are of opposite sign, and include $\mathrm{H} = 0$. This is the result given on p. 142 (save for a slight difference of notation). For $n = 3$, an analogous computation shows that q^2 is positive except when H is between

$$\tfrac{3}{4}k_1^2\lambda^2 - \mathrm{P}\lambda^3 \quad \text{and} \quad \tfrac{3}{4}k_1^2\lambda^2 + \mathrm{P}\lambda^3,$$

where

$$\mathrm{P} = \tfrac{9}{4}k_1^3 - 3k_1k_2 + k_3,$$

and this range does not include $\mathrm{H} = 0$ unless $k_1 = 0$. It would appear, from the formula above (p. 184), that the corresponding interval for greater integer values of n is between two quantities of the forms

$$\frac{2n}{n^2-1}\,k_1^2\lambda^2 + \mathrm{P}\lambda^3, \quad \frac{2n}{n^2-1}\,k_1^2\lambda^2 + \mathrm{Q}\lambda^3.$$

Mr. E. LINDSAY INCE, of Trinity College, Cambridge, following up the method of his paper referred to above (footnote, p. 134), has calculated numerical results for the case when k_1, k_2, ... have the values considered by G. W. HILL.]

PART III.

§ 22. I desire to add to the foregoing some very incomplete remarks in regard to a generalisation of which the work appears to be capable. The most important general result obtained is that when u is a periodic matrix, the matrix $\Omega(u)$ can be expressed as a periodic matrix P multiplied into a matrix involving quantities of the form $e^{\lambda\tau}$. One direction in which this result can be amplified is by extending the assumption we have made that the matrix $\Omega_0^{w}(u)$ has linear invariant factors. It is well enough understood what is the character of the modifications thereby introduced. A more important generalisation appears to be that the factorisation of the matrix $\Omega(u)$ does not in fact require that u be a periodic matrix. As an indication of the theorem consider an equation

$$\frac{d^2x}{dt^2}+\sigma^2x = x\,(ae^{i\kappa t}+be^{i\lambda t}+ce^{i\mu t}),$$

in which the constants κ, λ, μ are such that $\kappa+\lambda+\mu = 0$, but the ratio of two of them at least is irrational. For example, we might have $\kappa = \sqrt{2}+1$, $\mu = -\sqrt{2}+1$, $\mu = -2$. Then, assuming that there exists no identity of the form

$$\alpha\kappa+\beta\lambda+\gamma\mu\pm 2\sigma = 0,$$

in which α, β, γ are positive integers, the equation would seem to have a solution of the form

$$x = e^{iqt}\mathrm{X},$$

where X is a series of positive and negative integral powers of $e^{i\kappa t}$, $e^{i\lambda t}$, $e^{i\mu t}$, $e^{i\sigma t}$, which may be arranged as a power series in a, b, c, and q is a series of the form

$$q = \sigma+\mathrm{A}_1abc+\mathrm{A}_2a^2b^2c^2+\dots,$$

in which A_1, A_2, ... are constants. The differential equation has not periodic coefficients.

In a paper already far too often referred to, 'Proc. Lond. Math. Soc.,' XXXV., 1902, p. 353 *et seq.*, replacing the variable there called t by e^{τ} or ζ, it is shown (p. 365) for the equation system

$$\frac{dx}{d\tau} = (\mathrm{A}+\zeta\mathrm{V})\,x, \quad = ux, \text{ say},$$

in which A is a matrix of constants, and V a series of positive integral powers of ζ, that there is a factorisation of the matrix $\Omega(u)$, in the form $\mathrm{P}\Omega(\phi)\gamma$, where P is a matrix whose elements are power series in ζ, and $\Omega(\phi)$ is calculated in regard to τ from a matrix

$$\phi = \begin{pmatrix} \theta_1, & c_{12}(\zeta/\zeta_0)^{\theta_1-\theta_2}, & c_{13}(\zeta/\zeta_0)^{\theta_1-\theta_3}, & . & . \\ . & \theta_2, & c_{23}(\zeta/\zeta_0)^{\theta_2-\theta_3}, & . & . \\ . & . & . & . & . \end{pmatrix},$$

while γ is a matrix of constants. Here $\theta_1, \theta_2, \ldots, c_{12}, c_{13}, \ldots$ depend solely on the invariant factors of the matrix A.

This result is obtained from the form of the matrix u as expressible by powers of ζ, without reference to the question of periodicity. It would seem that the argument there employed is capable of modification, the integrations being performed in regard to τ (which is $\log t$ of the paper referred to), so as to lead to the general theorem here contemplated.

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BY

C. CHREE, Sc.D., LL.D., F.R.S.,
SUPERINTENDENT, KEW OBSERVATORY.

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V. *Discussion of Kew Magnetic Data, especially the Diurnal Inequalities of Horizontal Force and Vertical Force, from Ordinary Days of the Eleven Years* 1890 *to* 1900.

By C. CHREE, *Sc.D., LL.D., F.R.S., Superintendent, Kew Observatory.*

Received November 25, 1915—Read January 27, 1916.

CONTENTS.

§ 1. IN 1901 the development of electrical traction in West London rendered it clear that unless conditions altered in an unexpected direction, no further magnetic records from Kew Observatory would be sufficiently free from artificial disturbances to be an altogether satisfactory medium for the minute study of phenomena such as the regular diurnal variation. The time seemed to have come for taking stock of the records obtained. The measurement of magnetic curves formed no regular part of the work at Kew Observatory until 1890. Prior to that date the Annual Reports contained only a summary of the results of the absolute observations. Since 1890 the programme of work has included the measurement of the magnetic curves for 5 "quiet" days a month. Until a few years ago these days were selected at Greenwich by the Astronomer Royal. Now they are selected under international auspices at De Bilt, the central station of the Meteorological Institute of the Netherlands. Since Kew Observatory was transferred to the Meteorological Office, diurnal inequalities have been published for each month of the year for D (declination) and H (horizontal force). Previously the inequalities published were

[Published March 28, 1916.

confined to the year, winter (October to March) and summer (April to September). Vertical force (V) and inclination (I) suffer more than D and H from artificial electric currents, and no inequalities have been published for them since 1901.

It was decided to begin by analysing the measurements that had already been made of the "quiet" day curves for an eleven-year period, 1890 to 1900. The necessary labour was almost entirely arithmetical, and it was completed with the aid of the Observatory staff without extraneous financial assistance. The results were embodied in a paper* published in 1903.

It had gradually been recognised that diurnal variations derived from quiet days are not identical with those derived from all days, or from all days but those of large disturbance. It became increasingly obvious that the Kew records would not be fully utilised until the study was extended to other than quiet days. The magnitude of the task was not at first fully realised, and the original programme seems to have embraced all the accumulated data, limiting the enquiry however in the first instance to the declination. At all events the list of Government Grants for 1903 to 1904 includes one of £82 10*s*. "to work up declination (magnetic) results obtained at Kew from 1857 to 1900." The work was practically confined to the 11 years 1890 to 1900, and the grant was exhausted before it was completed.

The curves were divided into "ordinary" and "disturbed." An ordinary day was one in which the general trend of the diurnal variation was clearly recognisable, so that when the trace was oscillatory it could be fairly replaced by a freehand pencil curve of moderate curvature.

It had been the practice, when sensible oscillations occurred on a selected quiet day, to smooth the curve, replacing it by a pencil trace, so the procedure adopted with the ordinary day curves was no innovation. Smoothing was, however, done much more extensively than had been the case with quiet curves, and in some instances it called for considerable exercise of judgment. To secure uniformity, it was always done by myself. Disturbed days were those in which there was so much irregularity that smoothing appeared too arbitrary a process. To a certain extent, no doubt, the allotment of a day to the disturbed list depended on the judge's condition, both physical and mental, at the moment. The attributes of a disturbed day were practically those of "character" 2 days under the international scheme 0 (quiet), 1 (moderately disturbed), and 2 (highly disturbed); and it is only necessary to consult the returns from similarly situated stations to recognise the importance of the personal element in the selection. The choice, in the present case, it should be remembered, was based entirely on the D curves. The total number of days assigned to the disturbed list in the 11 years was 209, or an average of 19 a year. The number varied, however, from 6 in 1890 to 39 in 1896. The results from the ordinary day D curves, excluding a few that were imperfect, were discussed in a paper†

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* 'Phil. Trans.,' A, vol. 202, p. 335.

† 'Phil. Trans.,' A, vol. 208, p. 205.

published in 1908. This paper was reprinted with the addition of an Appendix in the 'Collected Researches' of the National Physical Laboratory, vol. 5, 1909. The Appendix contains a list of the 209 disturbed days.

In 1908–9 a further grant of £100 from the Government Grant Committee enabled the measurement to be commenced of all the H and V curves for the period 1890 to 1900. A difficulty at once presented itself. While some of the 209 days, which had been classified as disturbed from consideration of the D curves alone, were quite ordinary so far as the H curves were concerned, other days which had been treated as ordinary from the point of view of the D curves were conspicuously disturbed from the point of view of the H curves. V is a much less disturbed element at Kew than D or H, and many of the V curves from the 209 days classified as disturbed could have been smoothed satisfactorily. The decision reached was to regard the 209 days already selected as representing disturbed conditions for all three elements. Diurnal inequalities were derived from these, and these only, as representative of disturbed conditions. In their case the curves were read absolutely unsmoothed, at exact hours G.M.T. Notwithstanding the large irregularities in individual days, diurnal inequalities were obtained of a fairly regular character.*

§ 2. Coming now to ordinary days, it was decided in the case of H to set aside the 209 days already mentioned, and in addition all days when the H curves were too disturbed to smooth, and to derive inequalities from the remainder. These were smoothed, when it seemed expedient, exactly in the same way as the D curves had been. In the case of V a different procedure was adopted. There was no single month in which a large majority of the curves could not be satisfactorily used without any smoothing. This being so, it seemed best to dispense with smoothing—which everyone admits is open to certain criticisms, while some dispute its necessity—though that entailed omitting a considerable number of days additional to the 209.

The discussion of D results hardly comes under the present memoir, but D enters with H into such quantities as the north and west components (N and W), which of necessity are treated here. Thus particulars of the number of days' traces actually used for the ordinary day D inequalities concern us as well as the corresponding data for D and H. It is simpler to enumerate the days not used than those used. This is done for individual years in Table I., and for the 12 months of the year in Table II. The total number of days in the 11 years, it should be remembered, was 4017.

Natural disturbance was not the sole cause of omission of days. A few of the days—10 in the case of H, 19 in the case of D and V—were omitted owing to imperfections in the records. One cause of imperfection, stoppage of the clock, affected the three elements alike. Another cause, insufficient gas supply, affected all to some extent, but while one trace might be invisible another might be measurable.

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* 'Phil. Trans.,' A, vol. 210, p. 271, and 'Collected Researches, National Physical Laboratory,' vol. 7, p. 1.

The H optical arrangements are the best, and it suffered least. The erection in 1892 of a new upper story to the Observatory, with iron girders, produced irregularities on several days, which could not be satisfactorily dealt with. There were various other discontinuities associated with movement of iron in the building, or with changes of sensitiveness in the vertical force magnetograph, which rendered the omission of certain days expedient. But, everything considered, the number of days' trace which could not be utilised was wonderfully small, a fact reflecting credit on the staff, especially Mr. T. W. Baker, who had charge of the magnetic instruments during the whole period concerned. It was judged important to have a complete set of values of the absolute daily range (maximum less minimum) during the period. The loss of a good many hours' trace necessarily introduces some uncertainty into the daily range, because one at least of the extreme values might fall during the time lost; but in many cases one can be reasonably sure that the range deduced from the part of the trace that is complete is the full range, or at least very approximately so. In all doubtful cases recourse was had to the corresponding Falmouth curves, which were kindly lent by Mr. E. Kitto, then Superintendent of Falmouth Observatory. In a few cases, while the ranges accepted were derived essentially from the Kew curves, a small correction was applied which was based on a comparison of the Kew and Falmouth curves. In a few other instances the range accepted was derived from the Falmouth curve alone. Experience showed that the agreement between Kew and Falmouth ranges was usually so close that the uncertainty thus introduced into monthly or similar mean values must be wholly negligible. Finally, there were two or three cases in which one of the traces during a magnetic storm had gone beyond the limits of registration at the same time both at Kew and Falmouth, or the latter trace was otherwise incomplete. In such a case there was nothing for it but to take the edge of the sheet as representing one of the extreme values. On one occasion, February 14, 1892, the estimate thus made of the D range was not impossibly a very appreciable underestimate, though hardly to the extent of exercising an effect of more than a few tenths of a minute in the monthly mean.

The number of days omitted from the ordinary day diurnal inequalities through imperfections of the trace was so small that we shall not be far wrong if we disregard them when comparing different months or years in Tables I. and II. The curves D, H or V, of the same year were dealt with at one time, while a considerable interval sometimes intervened between the consideration of two successive years. Thus Table II. is probably a more reliable index than Table I. to the fluctuation of disturbance in individual elements. Since, however, the D, H and V curves were considered at widely different times, when their indications in Table I. agree the result may be accepted with some confidence. The two quietest years were undoubtedly 1890 and 1900, the years of lowest sunspot frequency. The last seven months of 1900 contained no single day considered disturbed for any of the elements, and may be accepted as the quietest period of the 11 years. The year of largest sunspot frequency, 1893, though showing very large regular diurnal variations, was decidedly quieter than the adjacent years.

TABLE I.—Number of Days not included in "Ordinary."

Element.	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	11 years.
D	7	26	31	17	21	21	41	16	19	21	8	228
H	6	25	36	14	26	29	45	19	21	22	9	252
V	14	48	53	36	36	39	54	26	28	21	11	366

While 1892 and 1894 contained most of the outstanding magnetic storms, 1896 was remarkable for the persistence of disturbed conditions. A point to be remembered is that it is easier to recognise the general trend of the regular diurnal variation when the range is large than when it is small. Thus a disturbance sufficient to mask the regular diurnal variation when least—*i.e.*, at midwinter, in sunspot minimum—might prove no serious obstacle to smoothing curves at midsummer near sunspot maximum. Making all due allowance for the increased amplitude of the regular diurnal variation in summer, Table II. shows clearly that the annual variation of disturbance has a well marked double period, with minima at midwinter and midsummer, and maxima in March (or late February) and October. The maximum in Spring is the more prominent of the two.

TABLE II.—Number of Days not included in "Ordinary."

Element.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
D	22	26	32	17	18	7	12	11	19	30	20	14
H	26	26	34	19	18	8	13	18	21	29	24	16
V	40	42	45	31	28	19	23	25	30	37	26	20

The basis on which the curves were treated was largely determined by the fact that the D, H and V curves had to be considered at different times. If a careful consideration of the curves from all three elements had preceded all measurements, a common selection of ordinary days would probably have been made. As it is, a little more disturbance enters into the ordinary day H inequality than into that for V, and a little more into the D inequality than into that for H. This is most to be regretted perhaps in relation to the derived inequalities. The north component (N) and west component (W) inequalities depend on both D and H, while the total force (T) and inclination (I) inequalities depend on H and V. These inequalities, not improbably, differ slightly from what they would have been if derived from magnetographs recording N, W, T and I directly. The differences, however, cannot be serious, because all the largest disturbances naturally figured on each of the three lists.

§ 3. The full publication of magnetic data normally includes tables of the hourly values of three elements in absolute measure. Besides hourly measurements of the curves, this entails for each element a knowledge of the scale value and of the base value for each day. When a temperature correction is necessary, and the temperature alters sensibly throughout the day, it entails further a knowledge of the temperature coefficient and measurements of the temperature records at each hour. Two months' hourly values of a single element in ordinary type fill a quarto page. Thus full publication of 11 years' data would have filled 198 quarto pages simply with the hourly values of D, H and V. As there was no prospect of publication on this scale, and economy of effort was important, no more was done than was essential for the immediate object in view. So long as one can assume the base value constant for the whole of each day, or can adequately allow for its fluctuation by means of a non-cyclic correction, its value is immaterial, so far as the diurnal inequality is concerned. For simplicity, consider the case where no temperature correction is required. If the scale value can be treated as constant for the whole of a month, as was the case at Kew with rare exceptions, all that is necessary is to take the hourly measurements in millimetres, sum the hourly columns, divide the hourly sums by the number of days in the month, allow for non-cyclic change, find the algebraic excess of each hourly mean value over the corresponding mean for the 24 hours, and convert the inequality thus formed into C.G.S. units, through multiplication by the factor representing the equivalent in force of 1 mm.

When a temperature correction is required, the inequality of temperature for each month can be derived from the hourly measurements of the temperature curves. This is converted into force from a knowledge of the temperature coefficient, and the result is applied with appropriate sign as a correction to the inequality already obtained. There would be a great increase of labour, and no gain in accuracy, so far as the inequality is concerned, if each hourly value of the magnetic curve were corrected for temperature. A second and conclusive reason for not correcting individual hourly values was the fact that continuous records of temperature were not taken in the magnetograph room until 1895. This being so, a course was followed which at least reduced labour to a minimum. During the 11 years no change had been made in the magnetograph room, or in the programme of work done in it or adjacent parts of the building. There was thus no reason to suspect any considerable change in the thermal phenomena in the room, and evidence pointing to the same conclusion was derivable from the 3 or 4 daily readings from mercury thermometers under the glass shades covering the H and V magnets. It was thus decided to calculate mean diurnal inequalities of temperature, utilising the thermogram measurements made on magnetic quiet days from 1895 to 1900, and these were taken as applying to the whole 11 years. This attributes to each January, for instance, the same diurnal inequality of temperature, while it was no doubt larger in some Januarys than others. This procedure no doubt introduced slight errors into the inequalities for individual months of individual years, but these would tend to disappear in results from groups of years or from the whole 11 years.

The temperature correction of the H magnetograph is about $1{\cdot}7\gamma$ per 1° F., and the range of the temperature diurnal inequality in most months was under 1° F, so a difference of temperature lag of even 1 or 2 hours between the magnet and thermograph would have had little effect. The fluctuations of temperature in the magnetograph room from one day to the next are sometimes much greater than the range of the regular diurnal variation, and the comparison of the readings from the thermograph and mercury thermometer on the one hand, and the corresponding fluctuation in the base values derived from individual absolute observations on the other, afforded grounds for confidence that uncorrected effects of temperature in the H inequalities must be trifling. The V magnet has a much larger temperature coefficient—about $12{\cdot}5\gamma$ for 1° F.—and the range of the regular diurnal variation is considerably less in V than in H. Thus there is more reason to fear uncorrected temperature effect in the V inequalities. It is, however, mainly in the absolute daily range—*i.e.*, the difference between the highest and lowest values throughout the day—that temperature uncertainty comes in. Undoubtedly some individual daily ranges, especially those of V, suffered considerably from this cause. In the case of an element like V at Kew considerably affected by temperature, it is sometimes difficult to recognise the maximum or minimum. If the temperature change in the day has been large, the maximum force may come at quite a different hour from the maximum ordinate. It may be necessary to take half a dozen measurements of the force curve, with the corresponding thermogram measurements, before one can decide. This is especially true of quiet curves—and most V curves are quiet—at seasons when the regular magnetic diurnal variation is small. No temperature corrections, of course, were possible until 1895, and mean results based on a number of days would have been practically useless in dealing with individual days. It was accordingly decided to attempt no temperature corrections to absolute daily ranges, but to derive them from the magnetic curves as if these required no temperature correction.

The neglect of temperature could hardly prejudice one's view of the character of the day as quiet or disturbed, but undoubtedly in a few cases it led to a quiet day being assigned a V range more appropriate to a day of moderate disturbance. The neglect of temperature may even have exerted a slight effect on the estimate of the mean monthly value of the absolute range, as the occurrences of maximum and minimum are much more numerous at certain hours than others, and so the effect of the regular diurnal variation of temperature would not be wholly eliminated.

Non-cyclic Change.

§ 4. In obtaining the diurnal inequalities the non-cyclic (n.c.) change C—*i.e.*, the algebraic excess of the value at the second midnight (hour 24) over that at the first midnight (hour 0)—has been eliminated in the usual way, by applying at hour n the correction $C(12-n)/24$. In the case of D the value of C for each month of the eleven years was given in a previous paper.* The value $-0'.12$ assigned there to February, 1892, should have been $-0'.22$. Allowing for this, the mean values for the year 1892, for the month of February, and for the whole 11 years, become respectively $-0'.031$, $-0'.052$ and $-0'.301$. The change of force perpendicular to the magnetic meridian necessary to alter D by 1′ varied gradually from 5·29γ in 1890 to 5·36γ in 1900, the mean for the eleven years being 5·32γ. Tables III. and IV. give the mean yearly and monthly values of the n.c. change for the ordinary days in the three elements, those for D being expressed in terms of the equivalent force. Ordinary days, it should be noticed, include the quiet, though, of course, not the disturbed.

TABLE III.—Non-cyclic Change (Unit 0·01γ).

Element.	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	11 years.
D	− 7	−15	− 16	−23	−52	+ 4	− 16	−13	−25	−21	+ 9	−16·0
H	+ 2	+68	+200	+69	+90	+84	+118	+80	+63	+61	+42	+79·7
V	−37	−67	− 55	−55	−45	−40	− 25	−29	−30	−50	−28	−42·0

TABLE IV.—Non-cyclic Change (Unit 0·01γ).

Element.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
D	− 9	−28	− 41	− 6	+ 7	− 26	− 2	0	−52	− 24	− 15	+ 4
H	+ 41	+97	+202	+ 75	+ 49	+ 6	+ 54	+132	+64	+ 87	+ 84	+67
V	−115	+11	−122	−211	−219	−245	−126	− 2	+98	+214	+141	+73

There is obviously a prevailing tendency for the n.c. change on ordinary days to be negative in D and V and positive in H. The inference that the D and V elements were falling, and the H element rising, would be correct, though unwarranted. The n.c. effect is influenced, of course, by the secular change but it is partly of instrumental

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* 'National Physical Laboratory Collected Researches,' vol. V. (Table IIA., p. 48).

origin, and is partly dependent on the type of day dealt with. In the average of the ASTRONOMER ROYAL'S quiet days, D rose 0′·044 (0·23γ), H rose 3·34γ and V fell 0·84γ. Thus if all days had been quiet days, D and H would in a single year have increased respectively 16′·1 (86γ) and 1219γ, while V would have fallen 307γ. The real average annual changes during the eleven years were −5′·79 (−30·8γ) in D, +25·9γ in H and −22·6γ in V.

It seems desirable to look into the matter a little more closely. Take first the case of D. There were in the eleven years 209 disturbed and 19 incomplete days. None of the latter, so far as could be judged, were highly disturbed. If we regard them as ordinary, as we are fairly entitled to do, we have 3808 ordinary days. The mean observed n.c. changes on disturbed and ordinary days were respectively +0′·327 and −0′·0301. The total n.c. changes were thus +68′·3 on disturbed and −114′·6 on ordinary days, leaving a balance of −46′·3. If all measurements were exact, in the absence of instrumental change, we should expect this balance to agree with the observed secular change, but this at the observed average rate of −5′·79 per annum amounted to −63′·7. This leaves 16′·4 unaccounted for, suggesting an instrumental drift of 1′·5 per annum.

In the case of H the 10 incomplete days may reasonably be regarded as ordinary, making a total of 3775 ordinary days. The observed n.c. change on ordinary days averaging +0·797γ, the total n.c. change from the ordinary days of the eleven years comes to +3009γ. Of the remaining 242 days, 209 were included in the original list of disturbed days. The mean n.c. change for these days was −13·2γ, giving a total n.c. change of −2759γ. The remaining 33 days were included in the subsidiary list of disturbed days, which was made out when the H curves came to be treated. The sum of the n.c. changes on these 33 days was only −24γ. Thus the total n.c. change for the 4017 days of the eleven years was (+3009−2759−24)γ, or +226γ. The observed secular change, +25·9 × 11 or +285γ, exceeds this by only 59γ, suggesting the trifling instrumental drift of −5·4γ per annum.

In the case of V, including the incomplete amongst the ordinary days, we have 3669 of these with an average n.c. change of −0·420γ, giving a total of −1541γ. The 209 disturbed days in the original list contributed +209 × 2·7γ or +564γ, while the 139 disturbed days on the subsidiary list contributed +304γ. Thus for the whole 4017 days we have a balance of (−1541+564+304)γ or −673γ, as compared with a true secular change of −22·6 × 11γ or −249γ. This suggests an instrumental drift at the average rate of −39γ per annum.

The chief importance perhaps of these calculations is the light they throw on the trustworthiness of the magnetic curves and measurements. It is unnecessary to emphasise the fact that when instrumental creep is large it is a source of very considerable uncertainty. The results obtained above are not put forward as exact measures of the instrumental creep, but only as showing its order of magnitude and the general fact that it was small. Most of the quiet day curves were measured many years before the others, and a variety of scales were employed. Then the curves of the 209 originally selected disturbed days were not smoothed, while those of the ordinary days were. Thus in a good many cases, at the midnight common to a disturbed and an ordinary day two readings were taken, at widely different times, one on the unsmoothed curve, the other on a smooth pencil trace. In individual cases these two midnight readings differed considerably, and this of course influenced the balance of the n.c. changes. The difference between the n.c. changes in H on the 209 days of the original disturbed list and the supplementary list of 33 days may appear suspicious, but is easily accounted for. During a large magnetic storm H nearly always shows a slight rise at the start. This is usually followed by a fall, which goes on until the value has diminished below the normal, sometimes much below the normal. There is then a recovery, which may go on at a gradually diminishing rate for some days. The ends and beginnings of storms were represented by a larger proportion of the 33 than of the 209 days. One of the 33 days showed an n.c. change of $+140\gamma$.

In the case of D what the absolute observations suggested was not a real instrumental drift, but occasional small discontinuities due probably to movements of iron in the building. In the case of H there is confirmatory evidence from the base line values that the instrumental creep is in the direction simulating a fall of force, but they suggest -15γ per annum as a more probable estimate than -5γ as found above. In the case of V the instrumental creep in reality seems to fluctuate in direction. When a sensible change of sensitiveness occurred in the course of the year, the tendency to creep seemed more apparent. On individual ordinary days the n.c. change in V is mainly a temperature effect. This may in fact be recognised in the figures given in Table IV. The four months April to July include most of the summer rise of temperature in the magnetograph room, the principal part of the annual fall taking place in the four months September to December. The mean daily n.c. changes during these two groups of months are by Table IV. :

From April to July $-2{\cdot}00\gamma$.
,, September to December $+1{\cdot}32\gamma$.

The two means will naturally include equal or approximately equal contributions from any regular source of drift which is independent of temperature, such for instance as might arise from gradual weakening of the magnet. If we ascribe the difference between the two four months' means obtained above solely to temperature, and take the known temperature coefficient, viz., $12{\cdot}5\gamma$ per 1° F., then assuming the rise and fall of temperature in the two groups of months equal, we find for its amount

$$(3{\cdot}32/2) \times (120/12{\cdot}5) = 16{\cdot}0 \text{ F.}$$

This is not far from the truth. The annual range in reality usually exceeded 20° F., but the rise usually began in February and continued throughout part of August.

The fall of temperature usually continued throughout January, but the readjustments of the magnetograph were usually made in that month leading to special uncertainties in the n.c. changes.

Diurnal Inequalities.

§ 5. The diurnal inequality of a magnetic element is in continuous variation with the season of the year; it also varies according to the development of sunspots, and it depends on the more or less disturbed character of the day. There are most likely other causes of variation; for instance, it seems unlikely that the diurnal variation at a particular station remains wholly unaffected by the secular change in the earth's magnetism. In deciding on the amount of detail advisable in the presentation of the facts, several conflicting considerations have to be allowed for. There is a great deal which in the present state of our knowledge must be regarded as accidental in the magnetic changes on any individual day. If we derive inequalities from the combination of a very limited number of days, a good deal of this "accidental" element will remain uneliminated. If, on the other hand, we combine a large number of days from the same year, the inequality is inevitably a blend of more or less conflicting characteristics. The extent to which this is the case differs at different seasons of the year. There is, for instance, much greater variation in the type and amplitude of the diurnal inequality in the five months November to March than in the five months April to August. If we have at our disposal the data from a large number of years, we can get smooth diurnal inequalities for individual seasons of the year a good deal shorter than a calendar month. This is what we should naturally do if our object were to examine in very minute detail the mode of variation of the diurnal inequality throughout the year. It is, however, open to the objection that it would produce a mass of detail which few readers if any could digest. The object in view moreover might be to some extent defeated by the influence of the sunspot relationship and secular change effects. Considerations of space must also be borne in mind. Diurnal inequalities for each of the 132 months of the eleven years—let alone shorter periods of the year—for H, V, N, W, T and I would have entailed printing an immense mass of figures. As a matter of fact, diurnal inequalities were calculated for H and V from each of the 132 months, but not for the other elements. The H and V ranges from these 132 inequalities are given later, but it was decided to publish for each of these elements only four tables of diurnal inequalities. Thus, in the case of H, Table V. gives the 12 diurnal inequalities obtained by combining all the months of the same name in the 11 years, three diurnal inequalities for the seasons winter (November to February), equinox (March, April, September and October) and summer (May to August), and finally the mean diurnal inequality for the whole year. Table VI. differs from Table V. only in that it is confined to the four years 1892 to 1895 representing large sunspot frequency; for brevity, it is described as referring to sunspot maximum. Table VII. is similarly confined to 1890, 1899, and 1900, and described as representing sunspot minimum. The mean values of WOLFER's sunspot frequency for the years included in these three tables were respectively 41·7, 75·0 and 7·2. Finally Table VIII. gives for each of the eleven years the mean diurnal inequality for the whole year. Tables IX. to XII. for V correspond exactly with the four tables for H. The n.c. element has been eliminated from all these tables in the way already described. All the inequalities refer to G.M.T. Kew local time is only $1\frac{1}{4}$ minutes after Greenwich, so the employment of local time would have made little difference.

§ 6. The other inequalities were calculated from the H, V and D inequalities, taking the latter as given in my previous paper. We have

$$T^2 = H^2+V^2, \quad \tan I = V/H, \quad N = H \cos D, \quad W = H \sin D \quad . \quad . \quad . \quad (1).$$

Thus if ΔT, ΔH, &c., represent corresponding small departures from the mean values we have

$$\left.\begin{aligned} \Delta T &= \cos I\, \Delta H + \sin I\, \Delta V, \\ \Delta I &= \tfrac{1}{2} \sin 2I\, (\Delta V/V - \Delta H/H), \\ \Delta N &= \cos D\, \Delta H - H \sin D\, \Delta D, \\ \Delta W &= \sin D\, \Delta H + H \cos D\, \Delta D \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

The coefficients of ΔH, ΔV, &c., on the right-hand sides of these equations varied slightly throughout the eleven years, in consequence of the secular change. They were treated as constant throughout individual years, and mean values were taken for inequalities based on the eleven years. In the latter case the formulæ actually used were

$$\left.\begin{aligned} \Delta T &= 0{\cdot}384\, \Delta H + 0{\cdot}923\, \Delta V, \\ \Delta I &= 0{\cdot}0277_5\, \Delta V - 0{\cdot}0668\, \Delta H, \\ \Delta N &= 0{\cdot}955\, \Delta H - 1{\cdot}58\, \Delta D, \\ \Delta W &= 0{\cdot}298\, \Delta H + 5{\cdot}08\, \Delta D \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

where the unit is $1'$ in the case of ΔI and ΔD, and 1γ in the case of the force elements.

Table XIII. gives diurnal inequalities for T. The results for the 12 months are from the 11 years combined. But in addition to a diurnal inequality for the year from the 11 years combined, there are corresponding inequalities for the sunspot maximum and minimum groups of years.

For I two inequality tables are given. Table XIV. contains inequalities for the 12 months and the whole year from the 11 years combined, being derived from Tables V. and IX. It also contains diurnal inequalities for the year from the sunspot maximum and minimum groups of years. Table XV. gives diurnal inequalities for the whole year, from the separate years, based on Tables VIII. and XII.

Tables XVI. and XVII. give monthly and seasonal diurnal inequalities for N and W from the whole 11 years, and diurnal inequalities for the year from the 11 years and the groups of years of sunspot maximum and minimum.

To save decimals $0{\cdot}1\gamma$ is employed as the unit in the tables relating to elements of force. The extreme hourly values, *i.e.*, the algebraic maximum and minimum, are in heavy type. In addition to the hourly values, the tables give the range or algebraic difference of the extreme hourly values, and the quantity described as A.D. (or average departure from the daily mean). The latter quantity represents the result obtained by dividing by 24 the numerical sum of the differences of the 24 hourly values from their arithmetic mean.

If readings were taken at every minute, instead of every hour of the day, larger values would in most cases be obtained for the range of the inequality, because it must be exceptional for the extreme values to fall at exact hours G.M.T. The under-estimate, however, thus arising is usually very small, as is easily recognised from the shape of the curves representing the inequalities. The value of the A.D. is naturally less affected by the accident of time, and in most cases it probably gives a better idea than the range of the activity of the forces to which the diurnal inequality is due. This is more especially the case when the inequality shows a double daily variation with two maxima and two minima.

§ 7. The inequality data in Table V. are shown graphically in fig. 1. As in other similar cases, the general features are most readily recognised in the curve, while for details recourse is desirable to the numerical data. Fig. 2 shows the H inequalities for the three seasons and the year, contrasting the data for the whole eleven years in Table V. with those for the sunspot maximum and minimum groups of years in Tables VI. and VII.

The composite character of the diurnal inequality in H derived from the whole year is most clearly seen by comparing some of the seasonal data in the morning hours in Table V. At 6h., for instance, while the winter value has its maximum for the day, the summer value falls below the daily mean. The transition from plus to minus in winter does not occur until nearly 9h., while it occurs in equinox shortly after 7 a.m., and in summer shortly after 5 a.m.

The minimum or principal minimum for the day occurs at 10h. from May to September, and at 11h. in the remaining seven months. It is the most constant and dominant feature in the inequality. In the four summer months the afternoon maximum—then the only maximum—is almost equally prominent, but in the other months the afternoon maximum resembles a plateau rather than a peak, and in the winter months the principal maximum occurs in the forenoon.

The forenoon maximum exists also as a secondary maximum in March and October, and even at midsummer the appearance of the curves suggests some influence delaying the plunge to the minimum at 10h. In most months the rise to the afternoon maximum seems to lag somewhat near 4 p.m., and a distinct secondary minimum is then recognisable in the case of January.

TABLE V.—Diurnal Inequality in Horizontal

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January	+ 3	+ 7	+ 19	+ 35	+ 57	+ **70**	+ 67	+ 39	− 17	− 63	− **90**	− 70
February	+ 17	+ 14	+ 16	+ 30	+ 50	+ 67	+ **69**	+ 41	− 21	− 78	−**112**	− 93
March	+ 46	+ 43	+ 45	+ 45	+ 58	+ **63**	+ 44	− 16	−109	−181	−**204**	−153
April	+ 74	+ 56	+ 50	+ 47	+ 46	+ 40	− 2	− 78	−178	−262	−**271**	−202
May	+ 60	+ 46	+ 36	+ 26	+ 8	− 31	− 97	−164	−213	−**235**	−214	−153
June	+ 52	+ 38	+ 33	+ 28	+ 6	− 47	−115	−181	−235	−**255**	−224	−162
July	+ 56	+ 42	+ 32	+ 25	+ 2	− 44	−107	−175	−235	−**262**	−238	−167
August	+ 81	+ 62	+ 57	+ 41	+ 15	− 23	− 98	−183	−247	−**266**	−225	−137
September	+ 78	+ 67	+ 61	+ 61	+ 55	+ 26	− 32	−117	−202	−**247**	−227	−135
October	+ 62	+ 60	+ 64	+ 74	+ **86**	+ 80	+ 49	− 26	−130	−207	−**213**	−165
November	+ 18	+ 22	+ 34	+ 48	+ 65	+ **75**	+ 65	+ 27	− 48	−105	−**122**	− 94
December	− 2	+ 3	+ 17	+ 34	+ 56	+ **72**	+ 67	+ 48	+ 6	− 41	− **64**	− 63
Winter	+ 9	+ 12	+ 22	+ 37	+ 57	+ **71**	+ 67	+ 39	− 20	− 72	− **97**	− 80
Equinox	+ 65	+ 57	+ 55	+ 57	+ 61	+ 52	+ 15	− 59	−155	−224	−**229**	−164
Summer	+ 62	+ 47	+ 39	+ 30	+ 8	− 36	−104	−176	−233	−**255**	−225	−155
Year	+ 45	+ 38	+ 39	+ 41	+ 42	+ 29	− 8	− 65	−136	−**184**	−**184**	−133

TABLE VI.—Diurnal Inequality in Horizontal Force,

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January	+ 21	+ 24	+ 36	+ 52	+ 71	+ **82**	+ 74	+ 38	− 30	− 93	−**125**	−111
February	+ 24	+ 23	+ 25	+ 39	+ 66	+ **86**	+ 81	+ 39	− 38	−107	−**149**	−128
March	+ 55	+ 55	+ 62	+ 64	+ 74	+ 77	+ 43	− 27	−137	−231	−**265**	−197
April	+ 97	+ 72	+ 64	+ 58	+ 52	+ 45	− 15	−104	−224	−332	−**335**	−250
May	+ 70	+ 50	+ 45	+ 34	+ 13	− 27	−104	−188	−254	−**285**	−269	−194
June	+ 61	+ 46	+ 41	+ 36	+ 8	− 59	−149	−241	−311	−**324**	−275	−194
July	+ 69	+ 55	+ 38	+ 29	− 6	− 61	−132	−212	−288	−**328**	−307	−219
August	+ 99	+ 77	+ 72	+ 56	+ 16	− 21	−115	−215	−292	−**318**	−282	−188
September	+ 95	+ 84	+ 73	+ 72	+ 64	+ 34	− 33	−133	−233	−**269**	−253	−163
October	+ 82	+ 84	+ 89	+ 99	+**111**	+100	+ 59	− 34	−159	−261	−**272**	−212
November	+ 35	+ 46	+ 58	+ 64	+ 81	+ **93**	+ 81	+ 29	− 65	−131	−**163**	−137
December	+ 9	+ 10	+ 24	+ 44	+ 67	+ **84**	+ 74	+ 53	0	− 58	− 94	− **95**
Winter	+ 22	+ 26	+ 36	+ 50	+ 71	+ **86**	+ 77	+ 40	− 33	− 97	−**133**	−118
Equinox	+ 82	+ 74	+ 72	+ 73	+ 75	+ 64	+ 13	− 75	−188	−273	−**281**	−205
Summer	+ 75	+ 57	+ 49	+ 39	+ 8	− 42	−125	−214	−286	−**314**	−283	−199
Year	+ 60	+ 52	+ 52	+ 54	+ 51	+ 36	− 11	− 83	−169	−228	−**232**	−174

Force, from 11 Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 29	− 5	− 7	− 16	− 12	0	+ 5	+ 4	0	+ 1	+ 1	+ 1	160	25·8
− 57	− 27	− 16	− 15	− 10	+ 1	+ 10	+ 21	+ 25	+ 24	+ 25	+ 21	181	35·8
− 87	− 32	+ 6	+ 21	+ 23	+ 37	+ 53	+ 60	+ 62	+ **63**	+ 60	+ 53	267	65·2
−125	− 47	+ 10	+ 50	+ 83	+165	+**112**	+110	+103	+ 98	+ 93	+ 89	383	97·1
− 93	− 32	+ 25	+ 74	+123	+154	+**164**	+143	+120	+100	+ 86	+ 72	399	102·9
− 95	− 21	+ 46	+ 90	+133	+165	+**183**	+168	+136	+107	+ 83	+ 67	438	111·3
− 91	− 14	+ 53	+ 95	+130	+156	+**169**	+162	+137	+111	+ 90	+ 71	431	111·0
− 58	+ 1	+ 40	+ 59	+ 80	+110	+**136**	+**136**	+127	+111	+ 95	+ 87	402	103·1
− 58	− 14	+ 5	+ 18	+ 35	+ 64	+ 89	+ 97	+ 95	+ 96	+ **98**	+ 86	345	86·0
−103	− 51	− 19	− 6	+ 16	+ 40	+ 53	+ 60	+ 65	+ 71	+ 72	+ 68	299	76·7
− 62	− 40	− 26	− 8	+ 12	+ 18	+ 21	+ 22	+ 20	+ 20	+ 18	+ 19	197	42·0
− 43	− 30	− 23	− 15	− 5	− 2	− 1	− 5	− 4	− 3	− 1	− 2	136	25·3
− 48	− 26	− 18	− 14	− 4	+ 4	+ 9	+ 10	+ 10	+ 11	+ 11	+ 10	168	31·6
− 93	− 36	0	+ 21	+ 39	+ 61	+ 77	+ **82**	+ 81	+ **82**	+ 81	+ 74	311	80·0
− 84	− 17	+ 41	+ 80	+117	+146	+**163**	+152	+130	+107	+ 89	+ 74	418	107·1
− 75	− 26	+ 8	+ 29	+ 51	+ 71	+ **83**	+ 81	+ 74	+ 67	+ 60	+ 53	267	67·6

from Sunspot Maximum Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 66	− 28	− 22	− 23	− 9	+ 8	+ 15	+ 16	+ 18	+ 19	+ 18	+ 15	207	42·2
− 87	− 52	− 25	− 10	+ 5	+ 18	+ 22	+ 30	+ 35	+ 34	+ 39	+ 30	235	49·7
−115	− 38	+ 10	+ 30	+ 35	+ 56	+ 71	+ 77	+ **80**	+ 78	+ 77	+ 66	345	84·2
−154	− 64	+ 6	+ 64	+102	+132	+**149**	+147	+133	+128	+117	+112	484	123·2
−124	− 49	+ 24	+ 88	+149	+188	+**201**	+176	+151	+125	+100	+ 82	486	124·6
−109	− 15	+ 68	+126	+175	+210	+**226**	+207	+168	+129	+ 97	+ 79	550	139·7
−124	− 27	+ 64	+125	+179	+209	+**219**	+202	+171	+137	+115	+ 92	547	142·0
− 98	− 8	+ 48	+ 78	+103	+137	+167	+**168**	+158	+137	+117	+105	486	128·1
− 81	− 32	− 5	+ 17	+ 37	+ 74	+102	+112	+109	+113	+**114**	+100	383	100·1
−135	− 71	− 25	− 1	+ 23	+ 52	+ 63	+ 75	+ 81	+ 84	+ 84	+ 85	383	97·5
−106	− 67	− 40	− 16	+ 8	+ 19	+ 29	+ 33	+ 42	+ 40	+ 34	+ 33	256	60·4
− 74	− 52	− 35	− 15	− 2	+ 2	+ 4	+ 8	+ 8	+ 13	+ 13	+ 12	179	35·4
− 83	− 50	− 30	− 16	0	+ 12	+ 17	+ 22	+ 26	+ 27	+ 26	+ 22	219	46·7
−121	− 51	− 4	+ 28	+ 49	+ 78	+ 96	+**103**	+101	+101	+ 98	+ 91	384	99·8
−114	− 25	+ 51	+104	+151	+186	+**203**	+188	+162	+132	+107	+ 90	517	133·5
−106	− 42	+ 6	+ 39	+ 67	+ 92	+**106**	+104	+ 96	+ 86	+ 77	+ 68	338	87·1

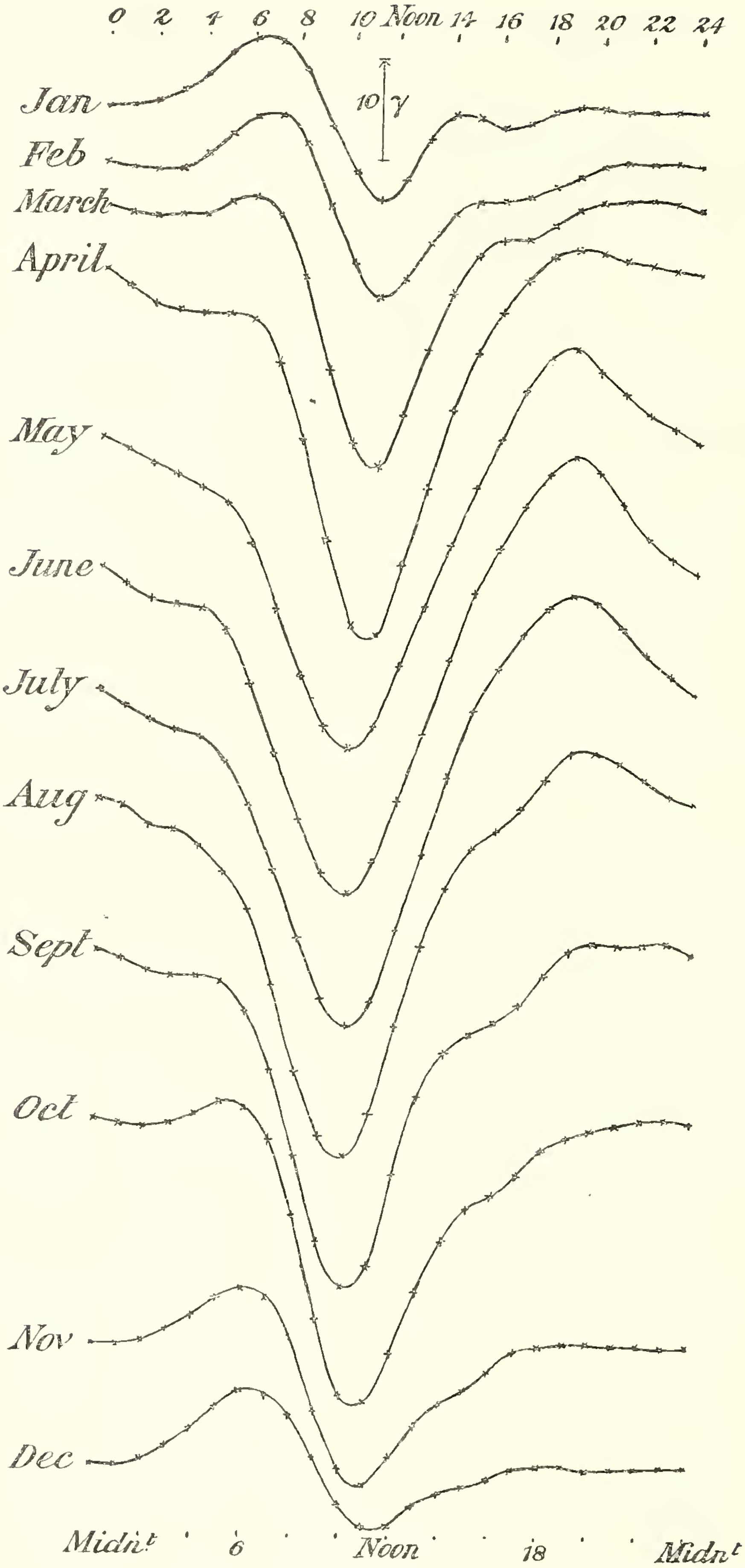

Fig. 1. Horizontal force. 11 years.

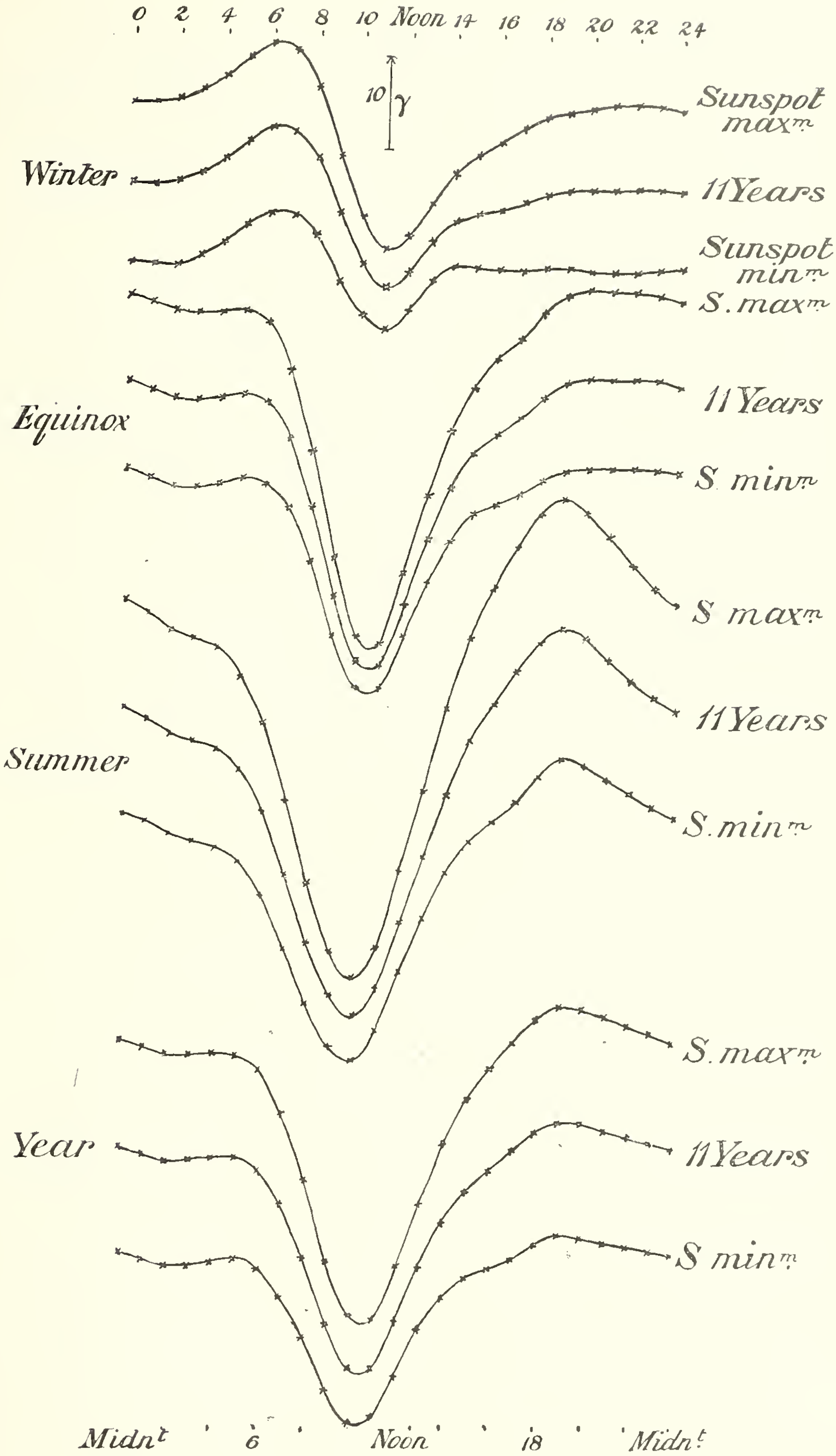

Fig. 2. Horizontal force.

TABLE VII.—Diurnal Inequality in Horizontal Force,

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 16	− 17	− 5	+ 9	+ 32	+ 47	+ **49**	+ 31	− 12	− 30	− **47**	− 17
February . .	+ 16	+ 7	+ 10	+ 20	+ 34	+ 48	+ **53**	+ 36	− 20	− 61	− **88**	− 69
March . . .	+ 31	+ 27	+ 29	+ 27	+ 41	+ **48**	+ 41	− 10	− 89	−143	−**157**	−112
April . . .	+ 55	+ 37	+ 29	+ 27	+ 28	+ 26	+ 5	− 47	−129	−195	−**198**	−145
May	+ 51	+ 42	+ 33	+ 23	+ 7	− 30	− 84	−137	−175	−**187**	−160	−108
June . . .	+ 45	+ 31	+ 24	+ 27	+ 15	− 22	− 76	−132	−182	−**208**	−185	−134
July	+ 48	+ 32	+ 22	+ 18	+ 5	− 32	− 89	−146	−194	−**204**	−173	−104
August . . .	+ 63	+ 53	+ 44	+ 30	+ 11	− 27	− 87	−154	−201	−**213**	−167	− 86
September .	+ 55	+ 46	+ 43	+ 49	+ 50	+ 24	− 25	− 94	−168	−**216**	−195	−105
October . .	+ 42	+ 43	+ 47	+ 55	+ **68**	+ 63	+ 39	− 21	− 98	−154	−**159**	−127
November . .	+ 5	+ 4	+ 18	+ 35	+ 53	+ **58**	+ 44	+ 17	− 41	− 84	− **87**	− 65
December . .	− 7	− 1	+ 12	+ 29	+ 50	+ **63**	+ 62	+ 47	+ 7	− 33	− **45**	− 39
Winter . . .	− 1	− 2	+ 9	+ 23	+ 42	+ **54**	+ 52	+ 33	− 17	− 52	− **67**	− 48
Equinox . .	+ 46	+ 38	+ 37	+ 40	+ 47	+ 40	+ 15	− 43	−121	−**177**	−**177**	−122
Summer . .	+ 52	+ 39	+ 31	+ 24	+ 9	− 28	− 84	−142	−188	−**203**	−171	−108
Year . . .	+ 32	+ 25	+ 25	+ 29	+ 33	+ 22	− 6	− 51	−108	−**144**	−138	− 93

TABLE VIII.—Diurnal Inequality in Horizontal

Year.	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
1890	+ 34	+ 25	+ 24	+ 29	+ 33	+ 19	− 10	− 52	−109	−**142**	−133	− 84
1891	+ 42	+ 37	+ 38	+ 43	+ 43	+ 25	− 11	− 67	−135	−**182**	−182	−134
1892	+ 61	+ 51	+ 49	+ 49	+ 39	+ 26	− 18	− 89	−174	−**232**	−231	−166
1893	+ 64	+ 56	+ 55	+ 59	+ 62	+ 41	− 9	− 86	−178	−244	−**251**	−187
1894	+ 60	+ 51	+ 55	+ 55	+ 54	+ 40	− 8	− 82	−169	−230	−**234**	−186
1895	+ 55	+ 51	+ 49	+ 52	+ 51	+ 37	− 10	− 75	−156	−206	−**213**	−157
1896	+ 44	+ 36	+ 36	+ 36	+ 41	+ 29	− 3	− 56	−129	−180	−**184**	−135
1897	+ 41	+ 33	+ 33	+ 37	+ 39	+ 32	+ 3	− 50	−110	−**160**	−159	−114
1898	+ 38	+ 32	+ 31	+ 34	+ 35	+ 21	− 10	− 61	−117	−**152**	−149	−105
1899	+ 36	+ 28	+ 27	+ 30	+ 35	+ 26	− 5	− 55	−117	−**154**	−147	−102
1900	+ 27	+ 23	+ 25	+ 29	+ 31	+ 22	− 3	− 46	−100	−**137**	−136	− 92

from Sunspot Minimum Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
+ 20	+ 32	+ 21	+ 1	− 17	− 10	− 9	− 9	− 14	− 14	− 12	− 11	96	20·1
− 30	− 2	+ 1	− 5	− 10	− 7	+ 2	+ 11	+ 15	+ 10	+ 15	+ 17	141	24·5
− 55	− 13	+ 17	+ 23	+ 17	+ 24	+ 34	+ 43	+ 44	+ 47	+ 44	+ 41	205	48·2
− 92	− 27	+ 22	+ 41	+ 60	+ 70	**+ 75**	**+ 75**	**+ 75**	+ 71	+ 68	+ 69	273	69·4
− 58	− 11	+ 26	+ 55	+ 89	+114	**+123**	+105	+ 92	+ 76	+ 66	+ 54	310	79·4
− 72	− 13	+ 31	+ 60	+ 89	+119	**+140**	+128	+106	+ 86	+ 68	+ 55	348	85·3
− 48	+ 5	+ 42	+ 61	+ 78	+104	**+123**	**+123**	+103	+ 90	+ 73	+ 61	327	82·4
− 22	+ 15	+ 34	+ 39	+ 46	+ 76	**+108**	+105	+101	+ 91	+ 77	+ 70	321	80·0
− 35	− 1	+ 13	+ 19	+ 31	+ 55	+ 79	**+ 80**	+ 74	+ 74	**+ 80**	+ 68	296	70·0
− 79	− 38	− 14	− 2	+ 16	+ 35	+ 42	+ 42	+ 47	+ 53	+ 50	+ 46	227	57·5
− 32	− 16	− 8	+ 6	+ 17	+ 21	+ 19	+ 11	+ 6	+ 6	+ 7	+ 8	145	27·8
− 14	− 11	− 13	− 11	− 4	− 3	− 13	− 23	− 19	− 15	− 9	− 9	108	22·5
− 14	+ 1	0	− 2	− 3	0	0	− 3	− 3	− 3	0	+ 1	121	17·9
− 65	− 20	+ 10	+ 20	+ 31	+ 46	+ 58	+ 60	+ 60	**+ 61**	+ 60	+ 56	238	60·4
− 50	− 1	+ 33	+ 54	+ 75	+103	**+123**	+115	+100	+ 86	+ 71	+ 60	326	81·3
− 43	− 7	+ 14	+ 24	+ 34	+ 50	**+ 60**	+ 58	+ 53	+ 48	+ 44	+ 39	204	49·2

Force, from Individual Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 34	0	+ 17	+ 29	+ 34	+ 48	**+ 56**	+ 51	+ 47	+ 41	+ 39	+ 38	198	47·0
− 73	− 20	+ 18	+ 35	+ 58	+ 76	**+ 80**	+ 76	+ 66	+ 60	+ 57	+ 50	262	67·0
−100	− 36	+ 10	+ 43	+ 72	+ 95	**+107**	+105	+ 99	+ 89	+ 81	+ 71	339	87·2
−110	− 38	+ 14	+ 47	+ 71	+ 92	**+105**	+104	+ 95	+ 87	+ 79	+ 73	356	92·0
−116	− 53	− 4	+ 35	+ 70	+101	**+114**	+112	+102	+ 89	+ 78	+ 66	348	90·2
− 97	− 41	+ 2	+ 30	+ 55	+ 81	**+ 97**	+ 96	+ 88	+ 80	+ 71	+ 61	310	79·6
− 77	− 29	+ 6	+ 27	+ 48	+ 69	+ 82	**+ 84**	+ 75	+ 68	+ 59	+ 53	268	66·1
− 67	− 32	− 6	+ 12	+ 40	+ 62	**+ 76**	+ 74	+ 63	+ 56	+ 53	+ 43	236	58·1
− 57	− 18	+ 3	+ 18	+ 39	+ 54	+ 71	**+ 72**	+ 66	+ 58	+ 52	+ 45	224	55·8
− 55	− 16	+ 8	+ 19	+ 36	+ 54	**+ 66**	+ 65	+ 61	+ 59	+ 55	+ 47	220	54·3
− 41	− 4	+ 17	+ 24	+ 33	+ 48	**+ 59**	+ 57	+ 50	+ 44	+ 38	+ 32	196	46·6

TABLE IX.—Diurnal Inequality in Vertical

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 6	− 10	− 16	− 18	− 19	− 20	− 23	− 25	− 30	− 36	− 33	**− 39**
February . .	− 8	− 20	− 24	− 19	− 21	− 23	− 23	− 23	− 31	− 61	**− 70**	− 61
March . . .	− 6	− 15	− 21	− 20	− 17	− 15	− 6	− 10	− 44	− 90	−126	**−127**
April . . .	+ 4	− 8	− 14	− 15	− 8	+ 2	+ 10	− 4	− 51	−106	−153	**−167**
May	+ 7	0	− 2	+ 2	+ 7	+ 6	− 10	− 35	− 85	−149	**−194**	−190
June . . .	− 5	− 19	− 20	− 14	− 8	− 16	− 25	− 51	− 84	−129	**−162**	−154
July	− 3	− 25	− 33	− 30	− 21	− 34	− 41	− 55	− 85	−115	−151	**−155**
August . . .	− 2	− 10	− 10	− 8	+ 4	+ 9	+ 6	− 13	− 59	−106	−143	**−147**
September. .	− 2	− 9	− 16	− 18	− 21	− 15	− 11	− 28	− 66	−106	**−127**	−122
October . .	− 8	− 14	− 23	− 24	− 26	− 25	− 15	− 10	− 31	− 72	**− 98**	− 89
November . .	− 15	− 20	− 23	− 23	− 22	− 27	− 31	− 25	− 31	**− 54**	**− 54**	− 37
December . .	− 3	− 12	− 15	− 17	− 13	− 12	− 13	− 16	− 23	**− 36**	− 34	− 35
Winter . . .	− 8	− 16	− 20	− 19	− 19	− 20	− 23	− 22	− 29	− 47	**− 48**	− 43
Equinox . .	− 3	− 12	− 18	− 19	− 18	− 13	− 6	− 13	− 48	− 94	**−126**	**−126**
Summer . .	− 1	− 13	− 16	− 13	− 5	− 9	− 17	− 38	− 78	−125	**−163**	−162
Year. . . .	− 4	− 14	− 18	− 17	− 14	− 14	− 15	− 25	− 52	− 88	**−112**	−110

TABLE X.—Diurnal Inequality in Vertical Force,

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 4	− 10	− 20	− 24	− 25	− 24	− 27	− 28	− 34	− 45	− 41	**− 50**
February . .	− 6	− 21	− 24	− 20	− 26	− 31	− 27	− 23	− 37	− 78	**− 88**	− 74
March . . .	− 17	− 22	− 34	− 30	− 22	− 18	0	0	− 38	− 90	−130	**−133**
April . . .	− 5	− 18	− 22	− 21	− 8	+ 8	+ 20	+ 7	− 46	−105	−160	**−178**
May	0	− 5	− 7	+ 3	+ 13	+ 13	− 5	− 35	− 91	−168	**−223**	−215
June . . .	− 16	− 28	− 28	− 18	− 6	− 10	− 20	− 53	− 89	−146	**−185**	−180
July	− 9	− 39	− 49	− 47	− 36	− 45	− 56	− 73	−102	−135	−171	**−178**
August . . .	− 5	− 13	− 15	− 13	+ 2	+ 10	+ 8	− 10	− 59	−115	−153	**−156**
September. .	− 5	− 11	− 18	− 23	− 26	− 19	− 13	− 31	− 73	−116	**−138**	−130
October . .	− 12	− 22	− 34	− 36	− 39	− 38	− 24	− 16	− 34	− 83	**−112**	−105
November . .	− 21	− 28	− 30	− 31	− 29	− 33	− 36	− 24	− 30	− 59	**− 62**	− 45
December . .	− 12	− 25	− 26	− 26	− 22	− 19	− 19	− 19	− 26	− 43	**− 46**	− 42
Winter . . .	− 11	− 21	− 25	− 25	− 26	− 27	− 27	− 24	− 32	− 56	**− 59**	− 53
Equinox . .	− 10	− 18	− 27	− 28	− 24	− 17	− 4	− 10	− 48	− 99	−135	**−136**
Summer . .	− 8	− 21	− 25	− 19	− 7	− 8	− 18	− 43	− 85	−141	**−183**	−182
Year. . . .	− 9	− 20	− 26	− 24	− 19	− 17	− 17	− 25	− 55	− 99	**−126**	−124

Force, from 11 Years. (Unit $0{\cdot}1\gamma$.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 23	+ 13	+ 33	+ 34	+ **40**	+ 39	+ 38	+ 38	+ 33	+ 18	+ 10	+ 2	79	24·8
− 44	− 4	+ 38	+ 60	+ **68**	+ 66	+ 57	+ 53	+ 41	+ 27	+ 16	+ 6	138	36·0
− 93	− 30	+ 38	+ 84	+**103**	+ 98	+ 89	+ 78	+ 63	+ 44	+ 19	+ 2	230	51·6
−132	− 51	+ 16	+ 59	+ 96	+**116**	+110	+ 97	+ 77	+ 58	+ 40	+ 23	283	59·0
−138	− 61	+ 9	+ 67	+115	+**142**	+139	+125	+ 98	+ 70	+ 50	+ 28	336	72·0
−109	− 43	+ 17	+ 75	+120	+141	+**142**	+127	+ 98	+ 64	+ 37	+ 19	304	70·0
−120	− 50	+ 24	+ 81	+128	+**154**	+149	+134	+106	+ 75	+ 45	+ 22	309	76·5
−107	− 38	+ 31	+ 74	+101	+**106**	+ 89	+ 80	+ 63	+ 45	+ 25	+ 9	253	53·5
− 78	− 16	+ 39	+ 81	+ **94**	+ **94**	+ 93	+ 82	+ 67	+ 50	+ 30	+ 8	221	53·0
− 57	− 11	+ 38	+ 69	+ **72**	+ **72**	+ 67	+ 65	+ 57	+ 38	+ 20	+ 6	170	42·0
− 15	+ 29	+ 53	+ **61**	+ 58	+ 52	+ 46	+ 38	+ 33	+ 15	+ 2	− 9	115	32·2
− 22	+ 5	+ 21	+ 32	+ **35**	+ 34	+ 31	+ 29	+ 28	+ 21	+ 13	+ 5	71	21·0
− 26	+ 11	+ 36	+ 47	+ **50**	+ 48	+ 43	+ 40	+ 34	+ 20	+ 10	+ 1	98	28·3
− 90	− 27	+ 33	+ 73	+ 91	+ **95**	+ 90	+ 81	+ 66	+ 47	+ 27	+ 10	221	51·1
−118	− 48	+ 20	+ 74	+116	+**136**	+130	+117	+ 91	+ 64	+ 39	+ 19	299	67·2
− 78	− 21	+ 30	+ 65	+ 86	+ **93**	+ 87	+ 79	+ 64	+ 44	+ 26	+ 10	205	48·6

from Sunspot Maximum Years. (Unit $0{\cdot}1\gamma$.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 35	+ 9	+ 34	+ 43	+ 49	+ 49	+ **51**	+ 49	+ 44	+ 23	+ 12	+ 4	101	30·6
− 52	− 3	+ 45	+ 69	+ **82**	+ 77	+ 71	+ 64	+ 47	+ 29	+ 19	+ 7	170	42·5
− 98	− 30	+ 44	+ 97	+**121**	+117	+100	+ 85	+ 63	+ 38	+ 7	− 10	254	56·0
−145	− 57	+ 13	+ 67	+107	+**126**	+120	+106	+ 83	+ 57	+ 37	+ 14	304	63·8
−159	− 78	+ 6	+ 72	+135	+**173**	+164	+146	+110	+ 76	+ 51	+ 24	396	82·2
−129	− 51	+ 24	+ 89	+146	+**169**	+164	+142	+109	+ 68	+ 35	+ 13	354	79·9
−141	− 53	+ 34	+104	+162	+**193**	+184	+164	+127	+ 89	+ 52	+ 25	371	94·5
−117	− 36	+ 34	+ 86	+**114**	+114	+ 95	+ 84	+ 64	+ 46	+ 24	+ 11	270	57·7
− 82	− 16	+ 48	+ 91	+**107**	+105	+102	+ 89	+ 72	+ 52	+ 30	+ 5	245	58·4
− 68	− 13	+ 51	+ 84	+ **97**	+ 95	+ 86	+ 81	+ 70	+ 43	+ 23	+ 6	209	53·0
− 24	+ 31	+ 63	+ **81**	+ 75	+ 65	+ 55	+ 46	+ 35	+ 11	0	− 10	143	38·5
− 27	+ 11	+ 33	+ 48	+ **50**	+ 45	+ 44	+ 44	+ 37	+ 25	+ 13	+ 2	96	29·3
− 34	+ 12	+ 44	+ 60	+ **64**	+ 59	+ 55	+ 51	+ 41	+ 22	+ 11	+ 1	123	35·0
− 98	− 29	+ 39	+ 85	+108	+**111**	+102	+ 90	+ 72	+ 48	+ 24	+ 4	247	56·9
−137	− 55	+ 25	+ 88	+139	+**162**	+152	+134	+103	+ 70	+ 41	+ 18	345	77·7
− 90	− 24	+ 36	+ 78	+104	+**111**	+103	+ 92	+ 72	+ 46	+ 25	+ 8	237	56·2

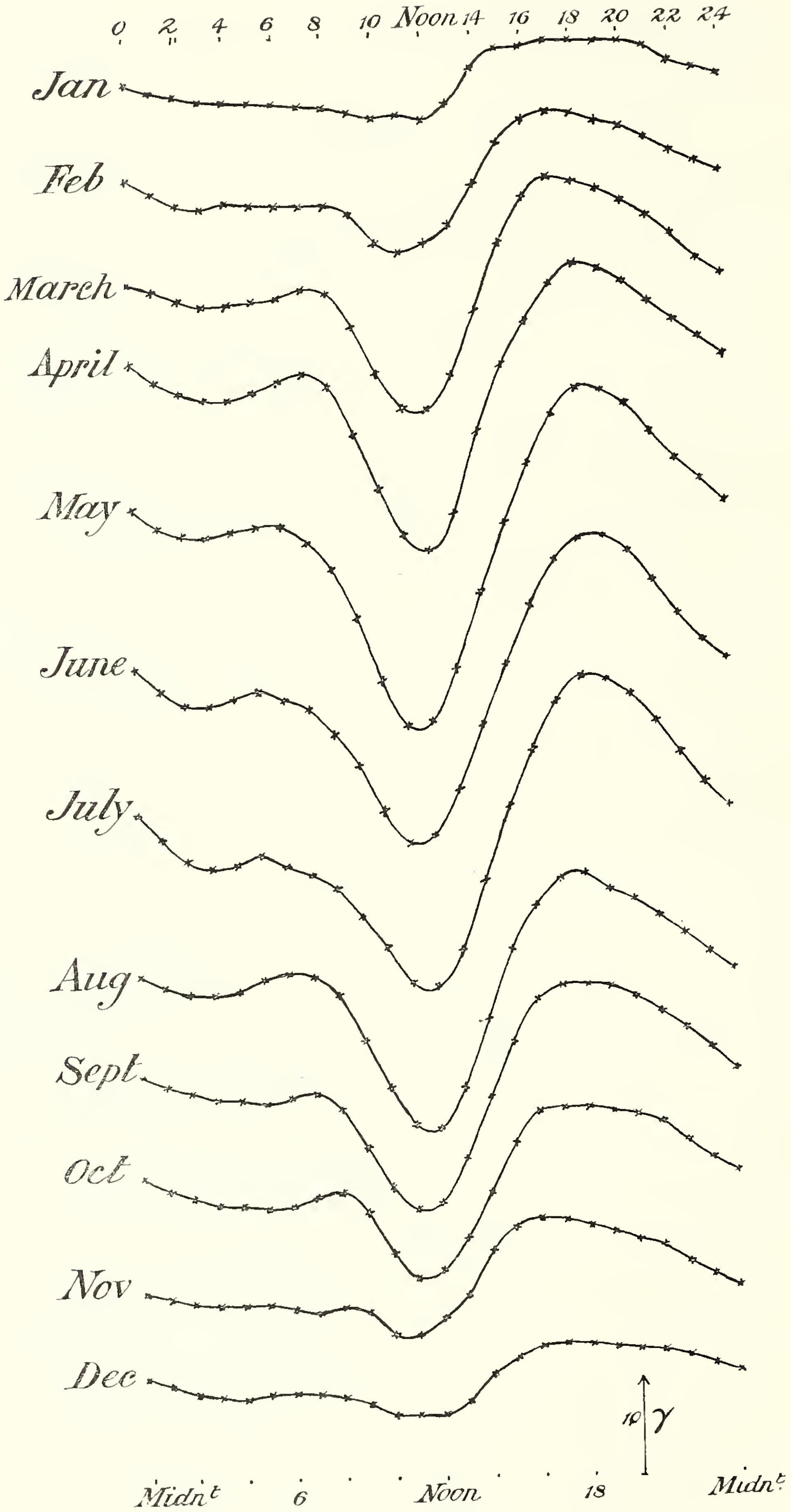

Fig. 3. Vertical force.

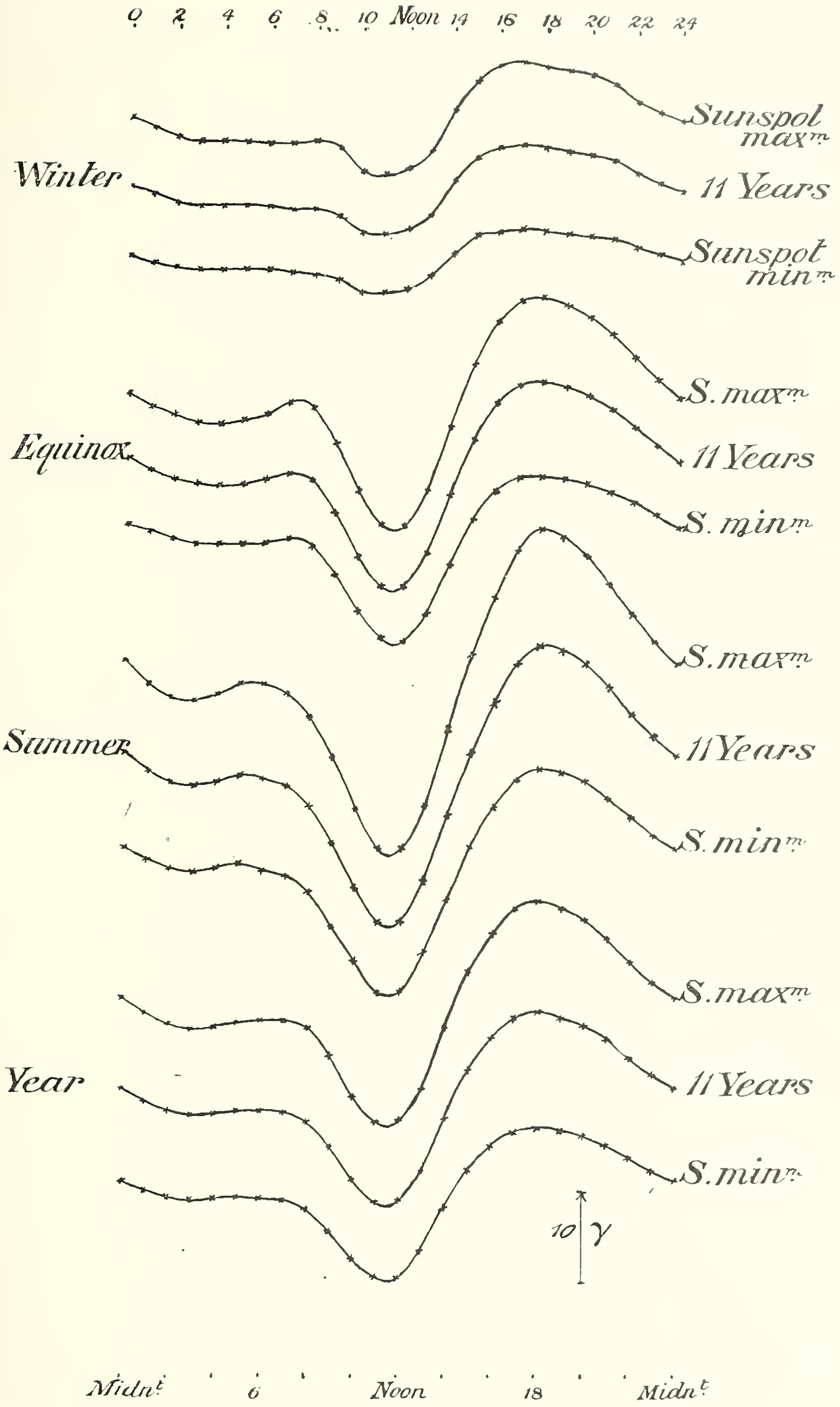

Fig. 4. Vertical force.

TABLE XI.—Diurnal Inequality in Vertical Force,

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 9	− 11	− 14	− 13	− 11	− 13	− 17	− 21	− 26	− **30**	− 25	− 28
February . .	− 8	− 16	− 21	− 18	− 16	− 16	− 17	− 20	− 25	− 43	− **49**	− 46
March . . .	+ 8	− 2	− 6	− 5	− 6	− 8	− 2	− 7	− 35	− 75	−108	**−113**
April . . .	+ 17	+ 7	+ 3	+ 3	+ 2	+ 5	+ 7	− 9	− 50	− 99	−140	**−154**
May	+ 18	+ 10	+ 2	+ 8	+ 9	+ 3	− 12	− 34	− 80	−127	−162	**−165**
June . . .	+ 2	− 10	− 9	− 4	− 4	− 14	− 20	− 39	− 70	−111	**−140**	−131
July	− 7	− 24	− 28	− 24	− 17	− 31	− 32	− 42	− 68	− 92	**−127**	−122
August . .	+ 3	− 1	− 2	+ 3	+ 15	+ 15	+ 12	− 6	− 48	− 86	−119	**−126**
September . .	0	− 5	− 9	− 8	− 11	− 8	− 3	− 19	− 52	− 86	**−108**	−105
October . . .	− 1	− 7	− 14	− 12	− 12	− 11	− 5	− 2	− 17	− 50	− **74**	− **74**
November . .	− 8	− 9	− 11	− 15	− 13	− 19	− 20	− 21	− 26	− **43**	− 42	− 28
December . .	+ 2	− 3	− 5	− 6	− 4	− 4	− 5	− 9	− 16	− **29**	− 25	− 27
Winter . . .	− 6	− 10	− 13	− 13	− 11	− 13	− 15	− 18	− 23	− **36**	− 35	− 32
Equinox . .	+ 6	− 2	− 7	− 6	− 7	− 5	− 1	− 9	− 39	− 78	−107	**−111**
Summer . .	+ 4	− 6	− 9	− 4	+ 1	− 7	− 13	− 30	− 67	−104	**−137**	−136
Year. . . .	+ 1	− 6	− 9	− 8	− 6	− 8	− 10	− 19	− 43	− 73	− **93**	− **93**

TABLE XII.—Diurnal Inequality in Vertical

Year.	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
1890	0	− 8	− 12	− 8	− 5	− 8	− 8	− 18	− 40	− 68	− 86	− **87**
1891	− 9	− 13	− 19	− 19	− 14	− 13	− 14	− 23	− 51	− 88	**−112**	−110
1892	− 16	− 25	− 32	− 28	− 21	− 21	− 22	− 32	− 57	− 95	**−123**	−122
1893	− 4	− 15	− 17	− 13	− 7	− 6	− 4	− 14	− 47	− 99	**−132**	−131
1894	− 8	− 19	− 27	− 28	− 25	− 22	− 21	− 28	− 60	−103	**−130**	−125
1895	− 9	− 21	− 26	− 25	− 22	− 20	− 20	− 27	− 56	− 97	**−119**	−118
1896	− 5	− 16	− 20	− 22	− 18	− 17	− 19	− 29	− 59	− 95	**−118**	−114
1897	+ 5	− 7	− 14	− 15	− 15	− 17	− 20	− 29	− 54	− 87	**−110**	−106
1898	− 3	− 12	− 17	− 14	− 12	− 15	− 19	− 32	− 58	− 90	**−110**	−107
1899	− 7	− 14	− 16	− 14	− 12	− 12	− 14	− 23	− 48	− 75	− **95**	− 94
1900	+ 11	+ 3	− 2	− 1	+ 1	− 5	− 7	− 16	− 40	− 73	− 99	**−100**

from Sunspot Minimum Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
– 12	+ 10	+ 32	+ 25	+ **33**	+ 29	+ 28	+ 30	+ 24	+ 14	+ 8	– 1	63	19·3
– 38	– 6	+ 30	+ 44	+ **49**	+ **49**	+ 43	+ 42	+ 35	+ 23	+ 18	+ 9	98	28·4
– 87	– 32	+ 26	+ 62	+ **75**	+ 68	+ 63	+ 58	+ 50	+ 39	+ 24	+ 11	188	40·4
–122	– 53	+ 3	+ 38	+ 75	+ **92**	+ 89	+ 81	+ 70	+ 57	+ 45	+ 31	246	52·2
–115	– 49	+ 9	+ 61	+ 94	+**108**	+107	+ 98	+ 81	+ 58	+ 45	+ 33	273	62·0
– 88	– 32	+ 10	+ 60	+ 93	+108	+**109**	+102	+ 79	+ 57	+ 35	+ 19	249	56·1
– 88	– 33	+ 28	+ 71	+105	+**121**	+117	+104	+ 83	+ 58	+ 33	+ 13	248	61·2
– 90	– 32	+ 27	+ 57	+ 76	+ **79**	+ 67	+ 58	+ 46	+ 30	+ 15	+ 5	205	42·4
– 64	– 8	+ 34	+ 64	+ **71**	+ 64	+ 66	+ 61	+ 52	+ 41	+ 28	+ 8	179	40·6
– 50	– 13	+ 26	+ **47**	+ 45	+ 46	+ 45	+ 43	+ 40	+ 28	+ 17	+ 7	121	28·6
– 5	+ 26	+ **42**	+ 39	+ 38	+ 35	+ 30	+ 23	+ 23	+ 9	0	– 9	85	22·2
– 14	0	+ 9	+ 16	+ **20**	+ **20**	+ 18	+ 15	+ 17	+ 15	+ 9	+ 5	49	12·2
– 17	+ 7	+ 28	+ 31	+ **35**	+ 33	+ 30	+ 28	+ 25	+ 15	+ 9	+ 1	71	20·2
– 81	– 27	+ 22	+ 53	+ 67	+ **68**	+ 66	+ 61	+ 53	+ 41	+ 29	+ 14	179	40·0
– 95	– 37	+ 19	+ 62	+ 92	+**104**	+100	+ 91	+ 72	+ 51	+ 32	+ 17	241	53·8
– 64	– 18	+ 23	+ 49	+ 64	+ **68**	+ 65	+ 60	+ 50	+ 36	+ 23	+ 11	161	37·5

Force, from Individual Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
– 61	– 15	+ 23	+ 47	+ 61	+ **65**	+ 62	+ 56	+ 46	+ 33	+ 22	+ 9	152	35·3
– 78	– 18	+ 30	+ 70	+ 89	+ **99**	+ 93	+ 79	+ 60	+ 38	+ 20	+ 4	211	48·5
– 84	– 19	+ 40	+ 80	+104	+**115**	+108	+ 97	+ 76	+ 50	+ 25	+ 2	238	58·1
–101	– 35	+ 31	+ 72	+ 99	+**102**	+ 94	+ 82	+ 66	+ 44	+ 25	+ 10	234	52·1
– 91	– 25	+ 33	+ 81	+109	+**117**	+108	+ 98	+ 76	+ 50	+ 30	+ 12	247	59·4
– 82	– 15	+ 39	+ 77	+103	+**109**	+103	+ 89	+ 69	+ 42	+ 21	+ 5	228	54·7
– 82	– 21	+ 33	+ 70	+ 91	+ **97**	+ 93	+ 86	+ 71	+ 50	+ 31	+ 13	215	52·9
– 77	– 28	+ 21	+ 54	+ 76	+ **87**	+ 84	+ 79	+ 68	+ 53	+ 33	+ 19	197	48·3
– 71	– 17	+ 30	+ 63	+ 82	+ **91**	+ 85	+ 77	+ 63	+ 45	+ 27	+ 12	201	48·0
– 63	– 17	+ 28	+ 55	+ 73	+ **79**	+ 77	+ 69	+ 56	+ 39	+ 21	+ 6	174	42·0
– 70	– 23	+ 18	+ 44	+ 59	+ **61**	+ 57	+ 53	+ 48	+ 36	+ 27	+ 18	161	36·3

TABLE XIII.—Diurnal Inequality in Total

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 4	− 7	− 8	− 3	+ 4	+ 8	+ 4	− 8	− 34	− 57	**− 65**	− 63
February . .	− 1	− 13	− 16	− 6	0	+ 4	+ 5	− 5	− 37	− 86	**−108**	− 92
March . . .	+ 12	+ 3	− 2	− 1	+ **7**	+ 10	+ 11	− 15	− 82	−153	**−195**	−176
April . . .	+ 32	+ 14	+ 6	+ 4	+ 10	+ 17	+ 8	− 34	−115	−198	**−245**	−232
May	+ 29	+ 18	+ 12	+ 12	+ 10	− 6	− 46	− 95	−160	−228	**−261**	−234
June. . . .	+ 15	− 3	− 6	− 2	− 5	− 33	− 67	−117	−168	−217	**−235**	−204
July	+ 19	− 7	− 18	− 18	− 19	− 48	− 79	−118	−169	−207	**−231**	−207
August . . .	+ 29	+ 15	+ 13	+ 8	+ 9	− 1	− 32	− 82	−149	−200	**−218**	−188
September .	+ 28	+ 17	+ 9	+ 7	+ 2	− 4	− 23	− 71	−139	−193	**−204**	−164
October. . .	+ 16	+ 10	+ 3	+ 6	+ 9	+ 8	+ 5	− 19	− 79	−146	**−172**	−146
November . .	− 7	− 10	− 8	− 3	+ 5	+ 4	− 4	− 13	− 47	− 90	**− 97**	− 70
December . .	− 4	− 10	− 7	− 3	+ 9	+ 16	+ 14	+ 4	− 19	− 49	− 56	− **57**
Year (11 years)	+ 14	+ 2	− 2	0	+ 3	− 2	− 17	− 48	−100	−152	**−174**	−153
Sunspot maximum	+ 15	+ 2	− 4	− 2	+ 2	− 2	− 20	− 55	−116	−179	**−205**	−181
Sunspot minimum	+ 13	+ 4	+ 1	+ 4	+ 7	+ 1	− 12	− 37	− 81	−123	**−139**	−121

TABLE XIV.—Diurnal Inequality

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
	′	′	′	′	′	′	′	′	′	′	′	′
January . .	−0·04	−0·07	−0·17	−0·28	−0·43	**−0·52**	−0·51	−0·33	+0·03	+0·32	**+0·51**	+0·36
February . .	−0·14	−0·15	−0·17	−0·25	−0·39	−0·51	**−0·52**	−0·34	+0·05	+0·35	**+0·55**	+0·45
March . . .	−0·32	−0·33	−0·36	−0·36	−0·43	**−0·46**	−0·31	+0·08	+0·61	+0·96	**+1·01**	+0·67
April . . .	−0·48	−0·40	−0·37	−0·36	−0·33	−0·26	+0·04	+0·51	+1·05	**+1·46**	+1·39	+0·89
May	−0·38	−0·31	−0·25	−0·17	−0·03	+0·22	+0·62	+1·00	**+1·19**	+1·16	+0·89	+0·49
June . . .	−0·36	−0·31	−0·28	−0·23	−0·06	+0·27	+0·70	+1·07	+1·34	**+1·35**	+1·05	+0·65
July	−0·38	−0·35	−0·31	−0·25	−0·07	+0·20	+0·60	+1·02	+1·33	**+1·43**	+1·17	+0·69
August . . .	−0·55	−0·44	−0·41	−0·30	−0·09	+0·18	+0·64	+1·19	**+1·49**	+1·48	+1·11	+0·51
September. .	−0·53	−0·47	−0·45	−0·46	−0·43	−0·22	+0·18	+0·70	+1·17	**+1·36**	+1·16	+0·56
October . .	−0·44	−0·44	−0·49	−0·56	**−0·65**	−0·60	−0·37	+0·15	+0·78	**+1·18**	+1·15	+0·86
November . .	−0·16	−0·20	−0·29	−0·38	−0·50	**−0·58**	−0·52	−0·25	+0·23	+0·55	**+0·67**	+0·53
December . .	+0·01	−0·05	−0·16	−0·27	−0·41	**−0·51**	−0·48	−0·37	−0·10	+0·17	**+0·33**	+0·32
Year (11 years)	−0·31	−0·29	−0·31	−0·32	−0·32	−0·23	+0·01	+0·37	+0·76	**+0·98**	+0·92	+0·58.
Sunspot maximum	−0·43	−0·40	−0·42	−0·43	−0·39	−0·29	+0·03	+0·49	+0·98	**+1·25**	+1·20	+0·82
Sunspot minimum	−0·21	−0·18	−0·19	−0·22	**−0·24**	−0·17	+0·01	+0·29	+0·60	**+0·76**	+0·66	+0·36

Force, from 11 years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
− 32	+ 10	+ 28	+ 25	+ 32	+ 36	+ **37**	+ 37	+ 31	+ 17	+ 10	+ 2	102	23·4
− 62	− 14	+ 29	+ 50	+ 59	+ **61**	+ 56	+ 57	+ 47	+ 34	+ 24	+ 14	169	36·7
−119	− 40	+ 37	+ 86	+104	+**105**	+103	+ 95	+ 82	+ 65	+ 41	+ 22	300	65·2
−170	− 65	+ 19	+ 74	+121	+**147**	+145	+132	+111	+ 91	+ 73	+ 55	392	88·3
−163	− 69	+ 18	+ 90	+153	+190	+**191**	+170	+137	+103	+ 79	+ 53	452	105·3
−137	− 48	+ 33	+104	+162	+193	+**201**	+182	+143	+100	+ 66	+ 43	436	103·5
−146	− 52	+ 43	+111	+168	+**202**	+**202**	+186	+150	+112	+ 76	+ 48	433	109·8
−121	− 35	+ 44	+ 91	+124	+**140**	+134	+126	+107	+ 84	+ 60	+ 42	358	85·5
− 94	− 20	+ 38	+ 82	+100	+111	+**120**	+113	+ 98	+ 83	+ 65	+ 40	324	76·0
− 92	− 30	+ 28	+ 61	+ 73	+ 82	+ 82	+ **83**	+ 78	+ 62	+ 46	+ 32	255	57·0
− 38	+ 11	+ 39	+ 53	+ **58**	+ 55	+ 51	+ 44	+ 38	+ 21	+ 9	− 1	155	32·3
− 37	− 7	+ 11	+ 24	+ 30	+ **31**	+ 28	+ 25	+ 24	+ 18	+ 12	+ 4	88	20·8
−101	− 30	+ 31	+ 71	+ 99	+**113**	+112	+104	+ 87	+ 66	+ 47	+ 30	287	66·6
−124	− 38	+ 35	+ 87	+122	+**138**	+136	+125	+103	+ 75	+ 53	+ 33	343	77·2
− 76	− 19	+ 27	+ 54	+ 72	+ 82	+ **83**	+ 78	+ 67	+ 52	+ 38	+ 25	222	50·7

in Inclination, from 11 Years.

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
′	′	′	′	′	′	′	′	′	′	′	′	′	′
+0·13	+0·07	+0·14	+0·20	+0·19	+0·11	+0·07	+0·08	+0·09	+0·04	+0·02	0·00	1·03	0·196
+0·27	+0·17	+0·21	+0·27	+0·26	+0·18	+0·09	−0·01	−0·05	−0·09	−0·12	−0·12	1·07	0·238
+0·32	+0·13	+0·07	+0·09	+0·13	+0·02	−0·11	−0·18	−0·24	−0·30	−0·35	−0·35	1·47	0·341
+0·47	+0·17	−0·02	−0·17	−0·29	−0·38	−0·44	−0·47	−0·47	−0·49	−0·51	−**0·53**	1·99	0·498
+0·24	+0·04	−0·14	−0·31	−0·50	−0·63	−**0·71**	−0·61	−0·53	−0·47	−0·44	−0·40	1·90	0·489
+0·33	+0·02	−0·26	−0·39	−0·56	−0·71	−**0·83**	−0·77	−0·64	−0·54	−0·45	−0·39	2·18	0·565
+0·27	−0·05	−0·29	−0·41	−0·51	−0·61	−**0·72**	−0·71	−0·62	−0·53	−0·48	−0·41	2·15	0·559
+0·09	−0·11	−0·18	−0·19	−0·25	−0·44	−0·66	−**0·69**	−0·67	−0·62	−0·57	−0·56	2·18	0·559
+0·17	+0·05	+0·07	+0·10	+0·03	−0·17	−0·34	−0·42	−0·45	−0·50	−**0·57**	−0·55	1·93	0·463
+0·53	+0·31	+0·23	+0·23	+0·09	−0·07	−0·17	−0·22	−0·28	−0·37	−0·43	−0·44	1·83	0·460
+0·37	+0·35	+0·32	+0·22	+0·08	+0·02	−0·01	−0·04	−0·04	−0·09	−0·11	−0·15	1·25	0·278
+0·23	+0·21	+0·21	+0·19	+0·13	+0·11	+0·09	+0·11	+0·10	+0·08	+0·04	+0·03	0·84	0·196
+0·28	+0·11	+0·03	−0·01	−0·10	−0·21	−0·31	−**0·33**	−0·32	−0·32	−**0·33**	−0·32	1·31	0·336
+0·46	+0·21	+0·06	−0·04	−0·16	−0·31	−0·42	−0·44	−0·44	−**0·45**	−**0·45**	−0·43	1·70	0·458
+0·11	0·00	−0·03	−0·02	−0·05	−0·15	−0·22	−0·22	−0·22	−0·22	−0·23	−0·23	1·00	0·233

Table XV.—Diurnal Inequality in

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
	′	′	′	′	′	′	′	′	′	′	′	′
1890	**−0·23**	−0·19	−0·19	−0·22	**−0·23**	−0·15	+0·04	+0·30	+0·62	**+0·76**	+0·65	+0·32
1891	−0·30	−0·28	−0·30	**−0·34**	−0·33	−0·20	+0·03	+0·38	+0·76	**+0·97**	+0·91	+0·59
1892	−0·45	−0·41	−0·41	−0·40	−0·32	−0·23	+0·06	+0·51	+1·00	**+1·29**	+1·20	+0·77
1893	−0·44	−0·41	−0·41	−0·43	−0·43	−0·29	+0·05	+0·54	+1·06	**+1·35**	+1·31	+0·88
1894	−0·42	−0·39	−0·44	−0·45	−0·43	−0·33	0·00	+0·47	+0·96	**+1·25**	+1·20	+0·90
1895	−0·39	−0·40	−0·40	**−0·42**	−0·40	−0·30	+0·01	+0·43	+0·89	**+1·10**	+1·09	+0·72
1896	−0·31	−0·28	−0·30	−0·30	**−0·32**	−0·24	−0·03	+0·29	+0·70	**+0·94**	+0·90	+0·58
1897	−0·26	−0·24	−0·26	−0·29	**−0·30**	−0·26	−0·08	+0·25	+0·58	**+0·82**	+0·75	+0·46
1898	−0·26	−0·25	−0·25	**−0·27**	**−0·27**	−0·18	+0·01	+0·32	+0·62	**+0·76**	+0·69	+0·40
1899	−0·26	−0·23	−0·22	−0·24	−0·27	−0·21	−0·01	+0·30	+0·65	**+0·82**	+0·71	+0·42
1900	−0·15	−0·15	−0·17	−0·20	−0·20	−0·16	0·00	+0·26	+0·55	**+0·71**	+0·63	+0·33

Table XVI.—Diurnal Inequality in North

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	+ 22	+ 23	+ 31	+ 45	+ 66	**+ 78**	+ 76	+ 51	− 6	− 66	**−112**	−111
February . .	+ 44	+ 36	+ 36	+ 48	+ 67	+ 83	**+ 84**	+ 59	− 2	− 74	−135	**−141**
March . . .	+ 72	+ 68	+ 70	+ 70	+ 83	**+ 89**	+ 78	+ 33	− 60	−158	**−227**	−222
April . . .	+ 93	+ 77	+ 73	+ 75	+ 79	+ 82	+ 56	− 8	−114	−231	**−291**	−275
May	+ 79	+ 69	+ 64	+ 62	+ 59	+ 33	− 22	− 91	−158	−220	**−248**	−229
June. . . .	+ 69	+ 60	+ 61	+ 68	+ 64	+ 28	− 32	−100	−171	−228	**−246**	−228
July	+ 74	+ 66	+ 61	+ 64	+ 60	+ 28	− 30	−101	−176	−236	**−257**	−232
August . . .	+104	+ 89	+ 88	+ 79	+ 65	+ 39	− 27	−114	−200	−259	**−267**	−224
September .	+104	+ 95	+ 92	+ 94	+ 90	+ 67	+ 18	− 63	−164	−245	**−272**	−220
October . .	+ 85	+ 81	+ 83	+ 91	**+103**	+ 98	+ 74	+ 13	− 88	−190	**−242**	−230
November . .	+ 38	+ 37	+ 45	+ 58	+ 75	**+ 85**	+ 76	+ 43	− 28	−101	**−144**	−140
December . .	+ 17	+ 16	+ 27	+ 40	+ 61	**+ 76**	+ 72	+ 54	+ 14	− 42	− 82	**− 98**
Winter . . .	+ 30	+ 28	+ 35	+ 48	+ 67	**+ 80**	+ 77	+ 52	− 6	− 71	−118	**−123**
Equinox . .	+ 89	+ 80	+ 79	+ 82	+ 89	+ 84	+ 56	− 6	−106	−206	**−258**	−237
Summer . .	+ 82	+ 71	+ 68	+ 68	+ 62	+ 32	− 28	−102	−176	−236	**−255**	−228
Year (11 years)	+ 67	+ 60	+ 61	+ 66	+ 73	+ 65	+ 35	− 19	− 96	−171	**−210**	−196
Sunspot maximum	+ 86	+ 80	+ 81	+ 86	+ 89	+ 81	+ 41	− 27	−121	−211	**−260**	−245
Sunspot minimum	+ 48	+ 40	+ 41	+ 48	+ 57	+ 51	+ 29	− 12	− 75	−135	**−163**	−149

Inclination, from Individual Years.

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
′	′	′	′	′	′	′	′	′	′	′	′	′	′
+0·06	−0·04	−0·05	−0·06	−0·06	−0·14	−0·20	−0·19	−0·19	−0·18	−0·20	**−0·23**	0·99	0·229
+0·27	+0·08	−0·04	−0·04	−0·14	−0·23	−0·28	−0·29	−0·28	−0·30	−0·32	−0·32	1·31	0·333
+0·44	+0·19	+0·04	−0·07	−0·19	−0·32	−0·42	−0·43	−0·45	−0·46	**−0·47**	**−0·47**	1·76	0·458
+0·45	+0·16	−0·01	−0·11	−0·20	−0·33	−0·44	**−0·47**	−0·45	−0·46	−0·46	−0·46	1·82	0·483
+0·52	+0·28	+0·12	−0·01	−0·16	−0·35	−0·46	**−0·48**	−0·47	−0·46	−0·44	−0·41	1·73	0·475
+0·42	+0·23	+0·10	+0·01	−0·08	−0·24	−0·36	−0·39	−0·40	**−0·42**	**−0·42**	−0·39	1·52	0·417
+0·29	+0·14	+0·05	+0·01	−0·07	−0·19	−0·29	**−0·32**	−0·30	−0·31	−0·31	**−0·32**	1·26	0·325
+0·23	+0·14	+0·10	+0·07	−0·05	−0·17	−0·27	−0·27	−0·23	−0·23	−0·26	−0·23	1·12	0·283
+0·18	+0·07	+0·06	+0·06	−0·03	−0·11	−0·24	−0·26	−0·26	−0·26	**−0·27**	**−0·27**	1·03	0·265
+0·19	+0·06	+0·03	+0·03	−0·04	−0·14	−0·22	−0·24	−0·25	−0·28	**−0·31**	−0·30	1·13	0·268
+0·08	−0·04	−0·06	−0·04	−0·05	−0·15	**−0·23**	**−0·23**	−0·20	−0·19	−0·18	−0·16	0·94	0·213

Component, from 11 Years. (Unit 0·1γ.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
−79	−47	−34	−35	−24	−5	+9	+18	+22	+27	+27	+25	190	43·3
−119	−89	−63	−43	−27	−8	+10	+31	+45	+51	+55	+52	225	58·4
−179	−123	−64	−20	+6	+32	+56	+69	+79	+85	+84	+79	316	87·8
−226	−146	−66	−1	+55	+95	+112	**+116**	+114	+114	+110	+107	407	113·2
−187	−123	−48	+22	+90	+137	**+158**	+143	+124	+108	+97	+87	406	110·8
−183	−115	−37	+26	+91	+139	**+168**	+159	+132	+107	+89	+79	414	111·7
−181	−109	−29	+35	+92	+134	**+156**	+153	+133	+112	+97	+83	413	112·5
−163	−97	−34	+16	+62	+105	+133	**+137**	+132	+121	+110	+106	404	115·5
−157	−101	−56	−15	+22	+60	+91	+106	+109	+114	**+120**	+111	392	107·7
−183	−124	−73	−36	0	+34	+57	+73	+86	+96	+99	+93	345	97·2
−116	−87	−58	−31	−2	+13	+25	+35	+42	+46	+45	+44	229	58·9
−86	−67	−50	−34	−15	−4	+6	+10	+18	+22	+24	+22	174	39·9
−100	−73	−51	−36	−17	−1	+13	+23	+32	+37	+38	+36	203	49·7
−186	−123	−65	−18	+21	+55	+79	+91	+97	+102	**+103**	+98	361	100·4
−179	−111	−37	+25	+84	+129	**+154**	+148	+130	+112	+98	+89	409	112·7
−155	−102	−51	−10	+29	+61	+82	**+87**	+86	+84	+80	+74	297	84·2
−198	−134	−67	−11	+38	+78	+102	**+109**	+108	+104	+99	+93	369	106·2
−111	−69	−30	−2	+21	+45	+61	**+64**	**+64**	+62	+60	+55	227	62·2

TABLE XVII.—Diurnal Inequality in West

	1h.	2h.	3h.	4h.	5h.	6h.	7h.	8h.	9h.	10h.	11h.	12h.
January . .	− 62	− 49	− 35	− 28	− 20	− 15	− 18	− 32	− 37	0	+ 55	+120
February . .	− 83	− 70	− 63	− 55	− 48	− 42	− 38	− 52	− 66	− 26	+ 57	+141
March . . .	− 75	− 73	− 73	− 74	− 72	− 72	−102	−158	**−173**	−102	+ 42	+197
April . . .	− 50	− 58	− 68	− 84	− 98	−127	−186	**−238**	−232	−140	+ 23	+204
May	− 52	− 67	− 84	−113	−163	−211	**−256**	−251	−208	− 84	+ 76	+221
June	− 47	− 64	− 86	−124	−187	−248	−284	**−288**	−242	−126	+ 35	+186
July	− 48	− 70	− 89	−121	−186	−238	−263	**−265**	−226	−124	+ 26	+182
August . . .	− 60	− 76	− 91	−114	−158	−204	−243	**−249**	−190	− 62	+100	+257
September . .	− 72	− 78	− 88	− 96	−103	−127	−165	**−190**	−154	− 43	+108	+252
October . .	− 64	− 58	− 52	− 44	− 41	− 46	− 73	−130	**−154**	− 86	+ 61	+184
November . .	− 61	− 44	− 31	− 25	− 21	− 21	− 24	− 49	− 71	− 31	+ 53	+134
December . .	− 60	− 44	− 28	− 14	− 7	− 2	− 5	− 13	− 26	− 2	+ 48	+104
Winter . . .	− 67	− 52	− 39	− 31	− 24	− 20	− 21	− 37	− 50	− 15	+ 53	+125
Equinox . .	− 65	− 67	− 70	− 75	− 79	− 93	−132	**−179**	−178	− 93	+ 59	+209
Summer . .	− 52	− 69	− 88	−118	−174	−225	−262	**−263**	−217	− 99	+ 59	+212
Year (11 years)	− 61	− 63	− 66	− 74	− 92	−113	−138	**−160**	−148	− 69	+ 57	+182
Sunspot maximum	− 76	− 81	− 85	− 94	−114	−138	−167	**−193**	−181	− 90	+ 54	+201
Sunspot minimum	− 45	− 44	− 47	− 57	− 73	− 91	−114	**−133**	−121	− 51	+ 58	+164

Component, from 11 Years. (Unit $0{\cdot}1\gamma$.)

13h.	14h.	15h.	16h.	17h.	18h.	19h.	20h.	21h.	22h.	23h.	24h.	Range.	A.D.
+157	+134	+ 87	+ 58	+ 37	+ 15	− 13	− 43	− 70	**− 84**	− 83	− 75	241	55·3
+190	**+195**	+148	+ 88	+ 54	+ 28	+ 1	− 27	− 60	− 81	− 92	**− 94**	289	75·0
+282	**+288**	+226	+134	+ 57	+ 23	− 2	− 21	− 45	− 60	− 67	− 76	461	103·9
+305	**+311**	+246	+170	+101	+ 47	+ 16	− 3	− 18	− 35	− 41	− 45	549	118·6
+287	**+288**	+239	+178	+125	+ 77	+ 46	+ 23	+ 6	− 9	− 23	− 37	544	130·2
+267	**+299**	+275	+220	+156	+109	+ 75	+ 55	+ 32	+ 16	− 6	− 27	587	143·9
+274	**+303**	+272	+207	+142	+ 94	+ 69	+ 53	+ 34	+ 14	− 9	− 29	568	139·1
+328	+315	+244	+147	+ 70	+ 34	+ 29	+ 18	+ 4	− 17	− 33	− 48	577	128·8
+309	+277	+195	+108	+ 48	+ 23	+ 8	− 13	− 31	− 44	− 57	− 68	499	110·7
+240	+226	+171	+ 97	+ 53	+ 26	− 3	− 33	− 58	− 71	− 75	− 70	394	88·2
+165	+144	+101	+ 72	+ 46	+ 19	− 8	− 39	− 69	− 82	**− 84**	− 77	249	61·3
+133	+115	+ 83	+ 58	+ 33	+ 6	− 22	− 48	− 71	**− 82**	− 81	− 77	215	48·4
+161	+147	+105	+ 69	+ 43	+ 17	− 10	− 39	− 67	− 82	**− 85**	− 81	246	60·0
+284	+276	+210	+127	+ 65	+ 30	+ 5	− 18	− 38	− 53	− 60	− 65	463	105·4
+289	**+301**	+258	+188	+123	+ 78	+ 55	+ 37	+ 19	+ 1	− 18	− 35	564	135·0
+245	+241	+191	+128	+ 77	+ 42	+ 16	− 7	− 29	− 45	− 54	− 60	405	98·2
+280	**+288**	+236	+167	+103	+ 60	+ 29	− 1	− 25	− 44	− 59	− 70	481	118·2
+213	+198	+144	+ 88	+ 46	+ 24	+ 8	− 10	− 27	− 39	− 45	− 46	346	78·6

As fig. 2 shows, the difference between sunspot maximum and minimum is mainly a matter of amplitude; but in winter, in particular, the tendency in the afternoon curves to a plateau—*i.e.*, the maintenance of a uniform value—is especially characteristic of sunspot minimum. Active regular changes in H at midwinter are mainly confined to the hours 2 a.m. to 2 p.m. Whether we consider the range or the A.D., December and January are clearly the months in which the diurnal inequality is least. In the case of the eleven years and the sunspot maximum group of years, the minimum is in December, but in the S minimum group it falls in January. The differences, however, between the two months are not so decisive as to justify the conclusion that what is true of this particular eleven years is invariably true. The sunspot minimum group in particular, it should be remembered, contained only three years. The maximum amplitude appears in June and July; but May and August are not far behind, especially in the sunspot minimum group of years. In sunspot maximum years April closely resembles May as regards range and A.D., but it exhibits a decided tendency to the evening plateau and morning minimum characteristic of winter. In sunspot minimum years April falls slightly behind September as regards amplitude, while September in all years falls markedly short of August and exhibits a distinct trace of the winter characteristics. These features, in conjunction with the desirability of having the same number of months in each season, seem to justify the division of months adopted. Any grouping which combined February with March, or October with November, seems less appropriate.

One or two features in Table VIII. call for remark. Whether we take the range or the A.D., the amplitude of the mean diurnal inequality for the year was greatest in 1893, the year of largest sunspot frequency, and least in 1890 and 1900, the years of least sunspot frequency. As will be seen presently, the inequality range and the sunspot frequency show a very close parallelism in their variation. The changes in the type of the inequality from year to year are small, and their elucidation requires a more sensitive method, such as the analysis into Fourier waves presently discussed. A tendency can, however, be recognised for the hour of the forenoon minimum to be slightly earlier when sunspots are few than when they are numerous.

§ 8. The V inequality data for the 12 months in Table IX. are shown graphically in fig. 3, while fig. 4 contrasts the diurnal inequalities for the seasons and the year derived from the whole eleven years and from the sunspot maximum and minimum groups of years, as given in Tables IX., X., and XI. The V inequality data are not quite so smooth as those for H, especially in winter. The fact that the H curves were smoothed, while the V curves were not, presumably partly accounts for this. The variation in the type of the inequality throughout the year is less in V than in H. In some months two distinct maxima and minima are visible in V, but the principal maximum always occurs in the afternoon between 4 p.m. and 7 p.m., while the principal minimum, in the forenoon, is as uniform in its time of incidence as the corresponding minimum in H. The time intervening between the morning minimum and afternoon maximum is less for V than for H, and, speaking generally, the preponderance in changes by day over those by night is greater in V. A further notable difference is that the season in which the double maximum and minimum are most in evidence is summer for V, but winter for H. Also the secondary maximum in the forenoon is in V most prominent at sunspot maximum, while in H it is most prominent at sunspot minimum. In winter the changes during the night hours are exceedingly slow in V as in H; but while the fall to the forenoon minimum is the conspicuous feature in H, it is the rise after the morning minimum that stands out in V. The minimum amplitude occurs as distinctly in December and January for V as for H. In V the lower value is found in December, both in sunspot maximum and minimum, especially the latter, again a difference from what we found in H. The smallness of the amplitude in V in December at sunspot minimum was, however, in considerable measure due to one year, 1890. During the last three months of that year the changes apparent in the V curves, regular and irregular alike, became so small that some defect in the magnetograph was suspected at the time, and the V data in the tables published in the Annual Report of the Kew Committee were confined to the first nine months of the year. There was, however, nothing but the smallness of the movements to suggest instrumental defect, and as the movements rapidly increased in 1891, without anything being done to the instrument, and the scale value determination showed nothing abnormal, the phenomenon was presumably real, and not of instrumental origin. As regards the month when the V inequality is largest, the decision depends upon what we accept as the criterion of amplitude. May comes distinctly first if we take the range, but if we take the A.D. July comes first in the case of the eleven years, and still more so in the case of the sunspot maximum group of years. August falls markedly short of the other summer months, and is inferior even to April.

Table XII. shows that in V, as in H, 1890 and 1900 were the years when the amplitude of the inequality was least; 1893, however, the year of sunspot maximum, was not the year of largest amplitude in V, being exceeded by 1892 and 1894, which were also much more disturbed. The difference in amplitude between years of many and few sunspots is less conspicuous in Table XII. than in Table VIII., and, as will be seen more clearly later, the parallelism between the amplitude of the inequality range and the development of sunspots was not so close in V as in H. Whether this last is a real natural phenomenon, independent of the lesser reliability of the V data in respect especially of temperature correction, is perhaps open to some doubt.

§ 9. If we write the first of equations (2), p. 198, in the form

$$T\,\Delta T = H\,\Delta H + V\,\Delta V,$$

and remember that at Kew $V = 2{\cdot}4H$ roughly, while the range of the diurnal inequality in V is about three-fourths that in H, we see at once that so far as diurnal changes are concerned, the influence of V on T very considerably exceeds that of H.

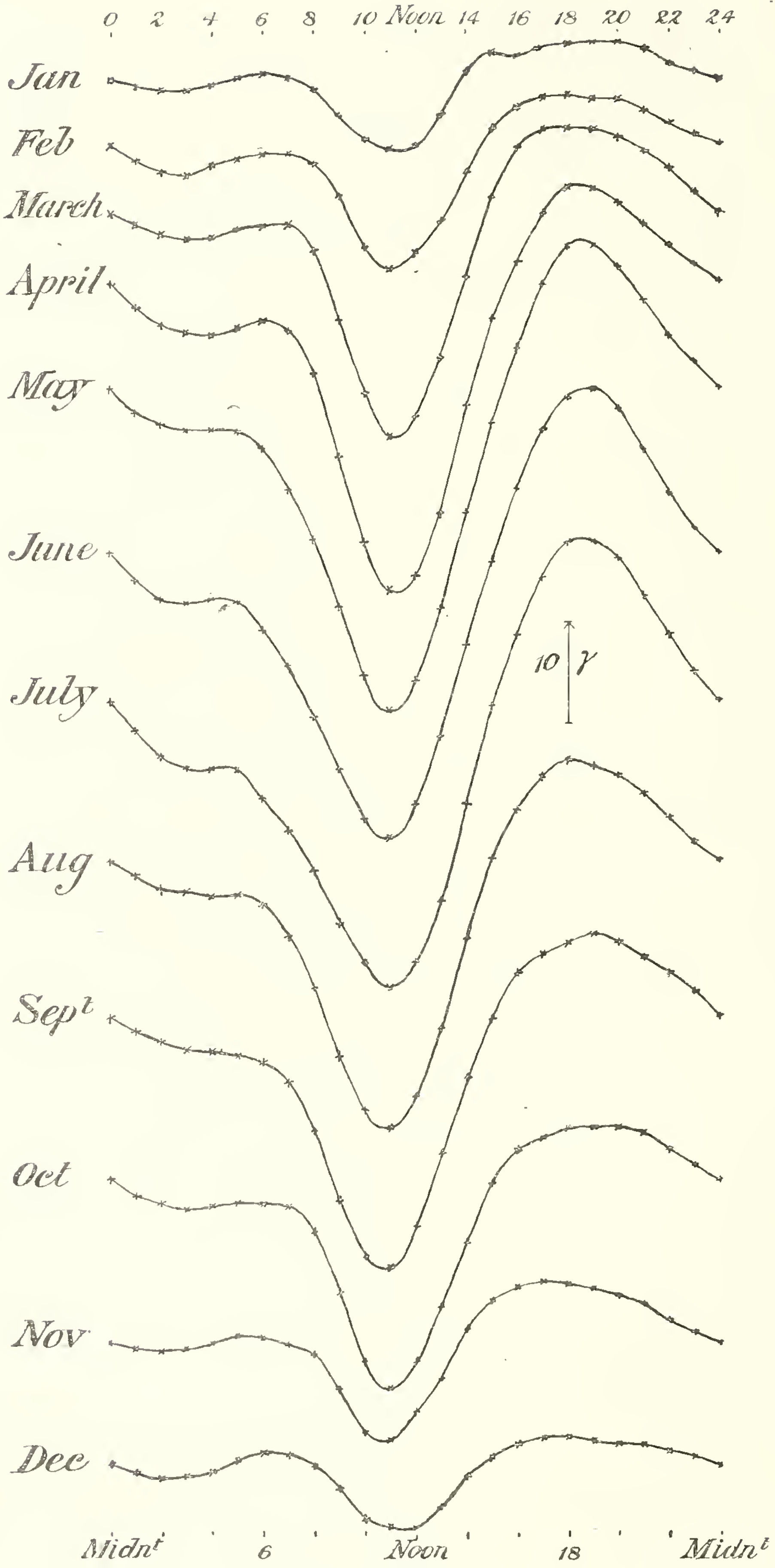

Fig. 5. Total force.

Also the diurnal inequalities in V and H follow a fairly similar course, thus we know *a priori* that the diurnal inequality in T must in general resemble somewhat closely that in V. In winter, however, the amplitude of the V inequality suffers a considerably larger relative reduction than that of H, and the difference of type between the inequalities in the two elements is then at its maximum. Thus we may expect the resemblance of the T to the V inequality to be less close in winter, and the influence of the H inequality to be then more apparent. The accuracy of these anticipations is readily recognised if we compare Table XIII. and fig. 5 with Table IX. and fig. 3.

Owing to the difference in type between the V and H inequalities in December and January, their contributions to the T inequality tend sensibly to neutralise one another. Thus the amplitude of the T inequality at midwinter is markedly less than that of H, while in June and July the amplitudes in the two elements are very similar. Consequently the variation in the range in the course of the year is decidedly more conspicuous in Table XIII. than in Tables V. or IX.

A conspicuous feature in Table XIII. is the uniformity in the time of occurrence of the principal minimum. It is shown at 11 a.m. in every month except December, when the 11 o'clock value just exceeds that for noon. The existence of a second minimum in the early morning is recognisable in most of the monthly curves of fig. 5; there is at least an arrest in the rate of change of the element. The maximum, or principal maximum, always occurs in the afternoon, usually from 6 to 7 p.m. Amongst the curves of fig. 7 are three contrasting the mean diurnal inequality in T for the year in the years of sunspot maximum and minimum and the average year. The variation of type with sunspot frequency makes little appeal to the eye.

§ 10. From the second of formulæ (2) or (3) connecting the I inequality with those for V and H, it appears that the contributions from V and H oppose one another, but that the H contribution must be largely dominant. The phases in the I and H inequalities are opposite, so a comparison of fig. 6, showing the inequalities in I, with fig. 1 does not at first sight show the dominance of H. A little consideration will, however, make this clear, if we remember the difference of phase. Answering to the prominent forenoon minimum in H, we have a prominent forenoon maximum in I, its time of occurrence being visibly earlier in summer than in winter. Again, as in H, there is a distinct difference of type between summer and winter. In summer, the principal or only minimum occurs in the afternoon, just as the principal maximum does in H; whereas in winter the principal minimum, like the principal maximum in H, is found in the morning.

In most months between 2 and 6 p.m. there is at least an arrest in the fall of I, just as there was an arrest in the rise of H. The opposition in phase between the I and T inequalities is readily recognised in fig. 7, where the curves from the two elements representing the mean diurnal variation for the year in the average year and in years of sunspot maximum and minimum are juxtaposed.

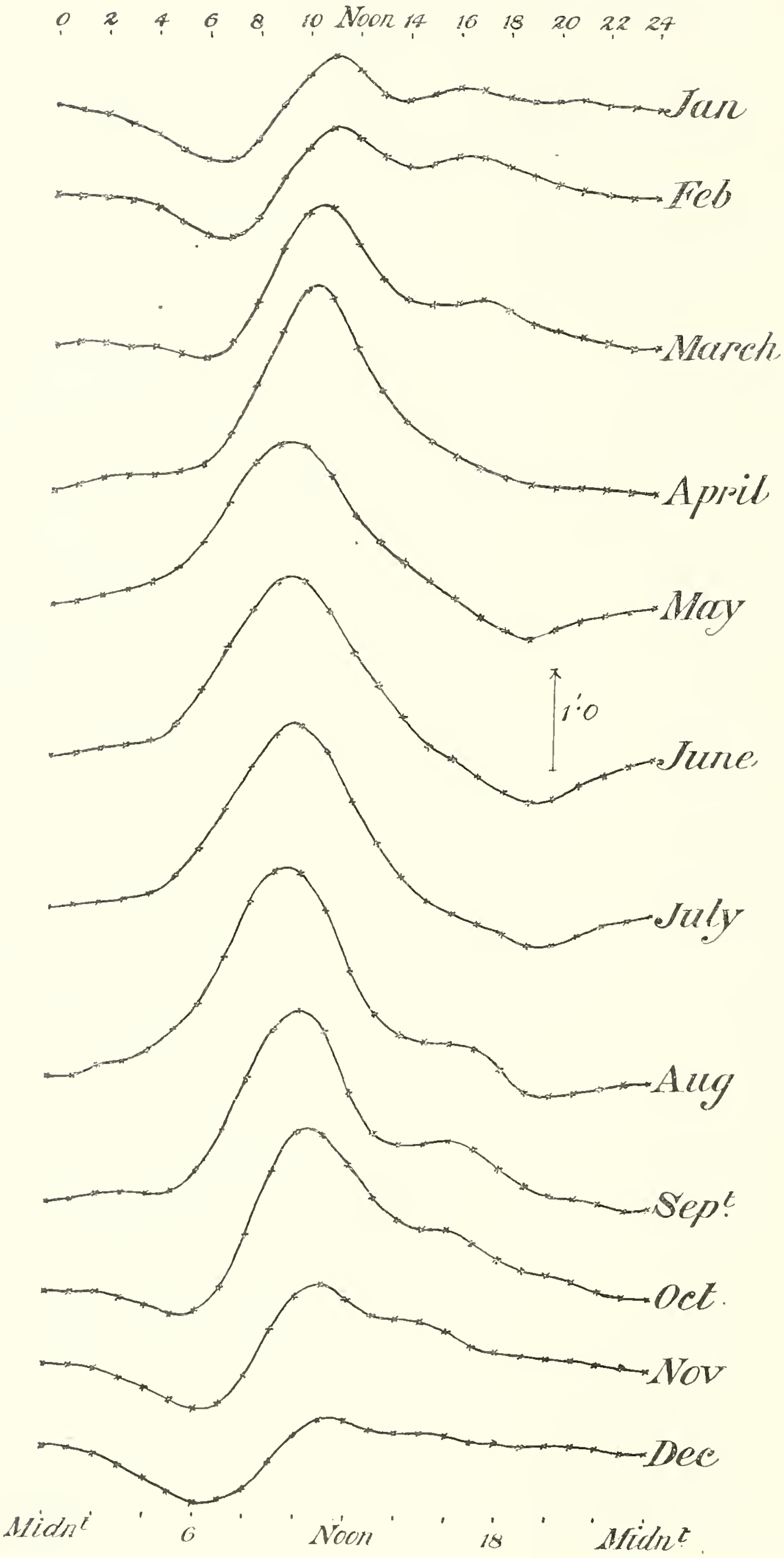

Fig. 6. Inclination.

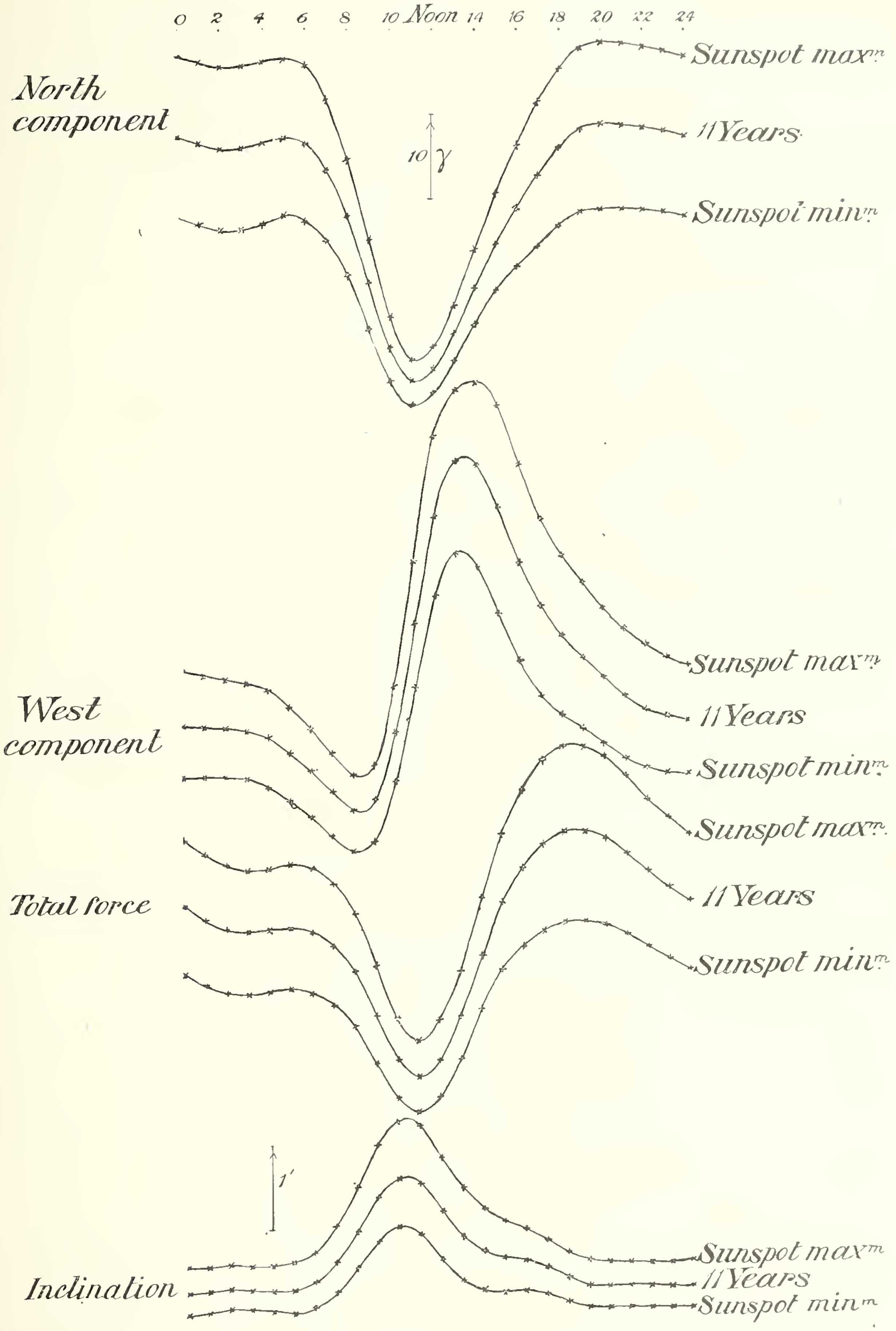

Fig. 7. Mean diurnal inequalities for the year.

The arrest in the afternoon fall of I, it will be seen, is more prominent at sunspot minimum than at sunspot maximum.

According to Table XIV., the December diurnal inequality in I has a decidedly smaller range than the January inequality, but the values of the A.D. for the two months are equal. In this case the August diurnal inequality markedly exceeds that for May, and is practically equal in amplitude to the June and July inequalities. The diminished amplitude of the May inequality in I is associated with the corresponding enhanced amplitude of the inequality in V. So far as amplitude is concerned, one would naturally group May with April, September and October. In amplitude March shows a closer approach to February than to April; in type it stands about equidistant from the two adjacent months.

§ 11. The graphical presentation of N and W diurnal inequalities, as given in Tables XVI. and XVII., is limited to the mean diurnal inequalities for the year from the eleven years and the groups of years of sunspot maximum and minimum. These are shown in the six uppermost curves of fig. 7.

If we take the mean diurnal inequality for the year, the range in H is only about three-fifths that in D, while cos D is three times sin D. It follows from the last of equations (2) that the influence of the D diurnal changes on W will largely exceed that of the H changes. Hence the diurnal inequality in W must show a fairly close approach in type to that in D. In the case of N the H diurnal changes exert more influence than the D changes, but the preponderance is less. As a matter of fact, however, there is a very close resemblance between the diurnal inequalities in H and N. The inequality in D if reversed has a considerable resemblance to that in H, and the contributions from H and D to the N diurnal inequality have opposite signs, so numerically they assist one another.

It is pretty obvious, comparing figs. 1 to 7, that if we measured east-west changes positive to the east, instead of to the west, and I changes positive from instead of towards the vertical, the diurnal inequality curves for the year in all the six elements considered here, and in D as well, would agree in having as one of their most prominent features a principal minimum occurring within an hour or two of noon.

According to Table XVI., the diurnal inequality in N is least in December, January coming next. June and July show the largest ranges, but there is little variation in that respect from April to September. August shows the largest A.D., April coming next. The six months April to September agree in having the maximum or principal maximum in the afternoon, while the other six months have it between 5 and 7 a.m.

Thus the phenomena in N rather favour the sub-division of the year into two seasons, each of six months. In March and October, however, while the forenoon maximum is the larger, it but very slightly exceeds the afternoon maximum, and the grouping of these months with the four midwinter months would be unsatisfactory.

According to Table XVII., December has distinctly the smallest amplitude in the diurnal inequality in W, January coming next. June shows the largest range and A.D., July coming decidedly next so far as A.D. is concerned, though slightly inferior to August as regards range. April closely resembles the midsummer months so far as range is concerned, but fall distinctly short of them in A.D. In this element the most conspicuous difference of type is between the four midwinter months, when the principal minimum occurs between 10 p.m. and midnight, and the other eight months when the principal minimum occurs between 7 and 9 a.m. The maximum, or principal maximum, is the pre-eminent feature. Like the corresponding maximum of westerly declination, it occurs between 1 and 2 p.m. the whole year round.

Comparing Tables XVI. and XVII., we see that the range of the mean diurnal inequality for the year in N is roughly three-fourths that in W; in winter and equinox, however, the fraction is distinctly larger. There is less difference between the values of A.D. in the two elements, especially in equinox.

§ 12. Figs. 8, 9 and 10 give the vector diagrams for the diurnal inequality forces in the horizontal plane. The arms of the cross are oriented in and perpendicular to the geographical meridian. The vector drawn from the centre of the cross, which serves as origin, to the points 1 to 24, represents in magnitude and direction the value at the hour specified of the horizontal component of the force to which the departure of the magnetic field from its mean value for the day may be ascribed. The scale of force is such that each arm of the cross represents 10γ. The vector travels completely round in the general clockwise direction in the course of the 24 hours. The motion is always direct between 6 a.m. and 10 p.m., but in the six months, October to March, there is a reversal of direction during some of the night hours. Details of this reversal are not clearly visible on the scale adopted in fig. 8, so they are shown on a more open scale in fig. 9, which is limited to part of the day.

The monthly diagrams in fig. 8 bring home to the eye the great variability in the type of the regular diurnal variation throughout the year. If the June and December diagrams were alone presented, it would be difficult to believe that they referred to the same physical entity. There are, however, some features common to all the diagrams. The time when the vector is directed due south falls in all cases between 10 and 11 a.m., and so is well in advance of the sun's crossing of the meridian. Again the vector in all cases has its maximum value near 1 p.m. The minimum value is usually seen near 6 p.m., but from April to July it occurs shortly after midnight.

The May, June, and July diagrams closely resemble one another. The August diagram differs from them in having a distinct bay in the afternoon hours, resembling in that respect the September and March diagrams. The diagrams for the midwinter months, November to February, have a pretty close family resemblance. If we take the months in their order, we can recognise a continuous development from January to May, and from July to December; but it is obvious that in some months, especially

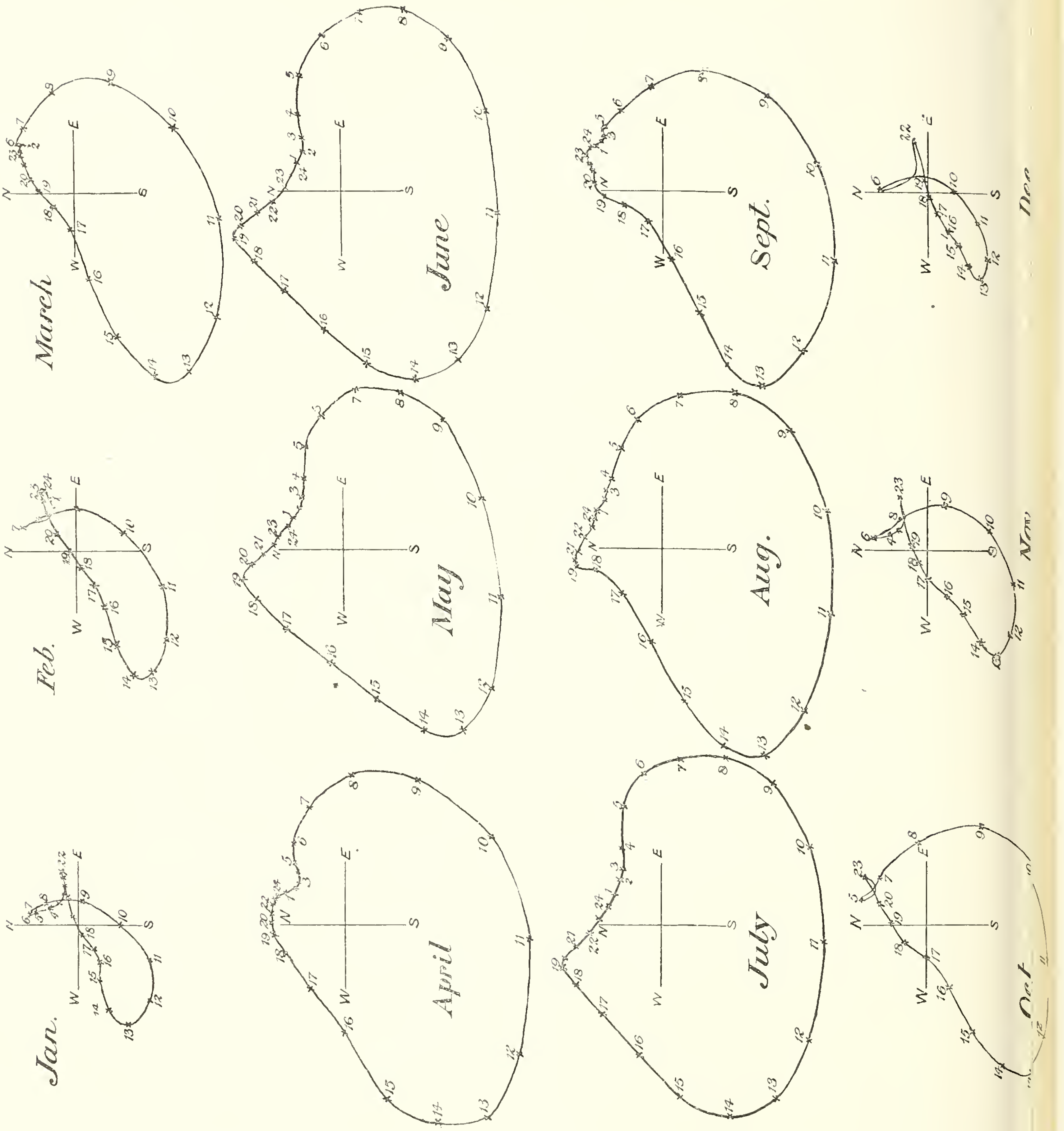

Fig. 8. Vector diagrams in horizontal plane (11 years). Arms of cross each 10γ.

in equinox, the amplitude and type at the beginning and end of the month must differ somewhat largely. The phenomena, for instance, near midnight must be considerably different in the beginning and end of March. What the March diagrams in figs. 8 and 9 show is a blend of different types. We want shorter periods than the calendar month if we are to trace the changes minutely.

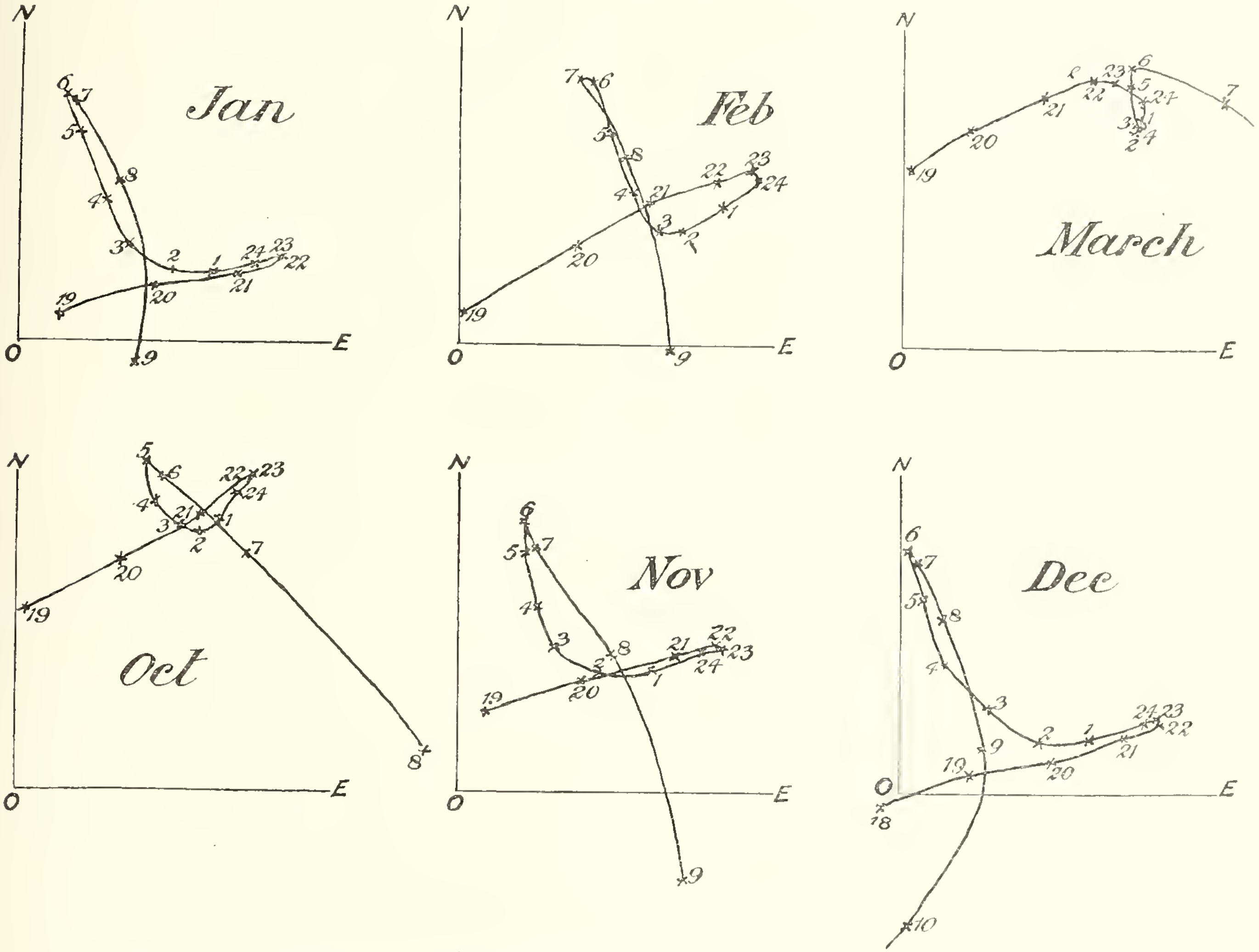

Fig. 9. Vector diagrams in horizontal plane. Details of variation near midnight (24h). (ON = OE $\equiv 10\gamma$.)

Fig. 10 shows the horizontal plane vector diagram for the year in the case of the whole eleven years, as well as in the cases of the sunspot maximum and minimum groups of years. The diagrams for the sunspot maximum and minimum groups of years are drawn from a common origin, as serving best to bring out points of agreement and difference. Except as regards the amplitude of the vector, the most noticeable difference between the sunspot maximum and minimum diagrams is that the indentation extending from about 11 p.m. to 5 a.m. is much more prominent in the latter. This indentation represents an approach to retrograde movement, a characteristic, as we have seen, of the winter season. Also, while a bay is recognisable in the afternoon hours in all three curves, it is deeper in the sunspot minimum diagram than in the other two.

The eye can recognise in fig. 10 that the sunspot minimum vector is in advance of the sunspot maximum vector from 10 a.m. to 10 p.m., the angular difference being considerable in the early afternoon. The vector has, however, its maximum near 1 p.m. in both cases.

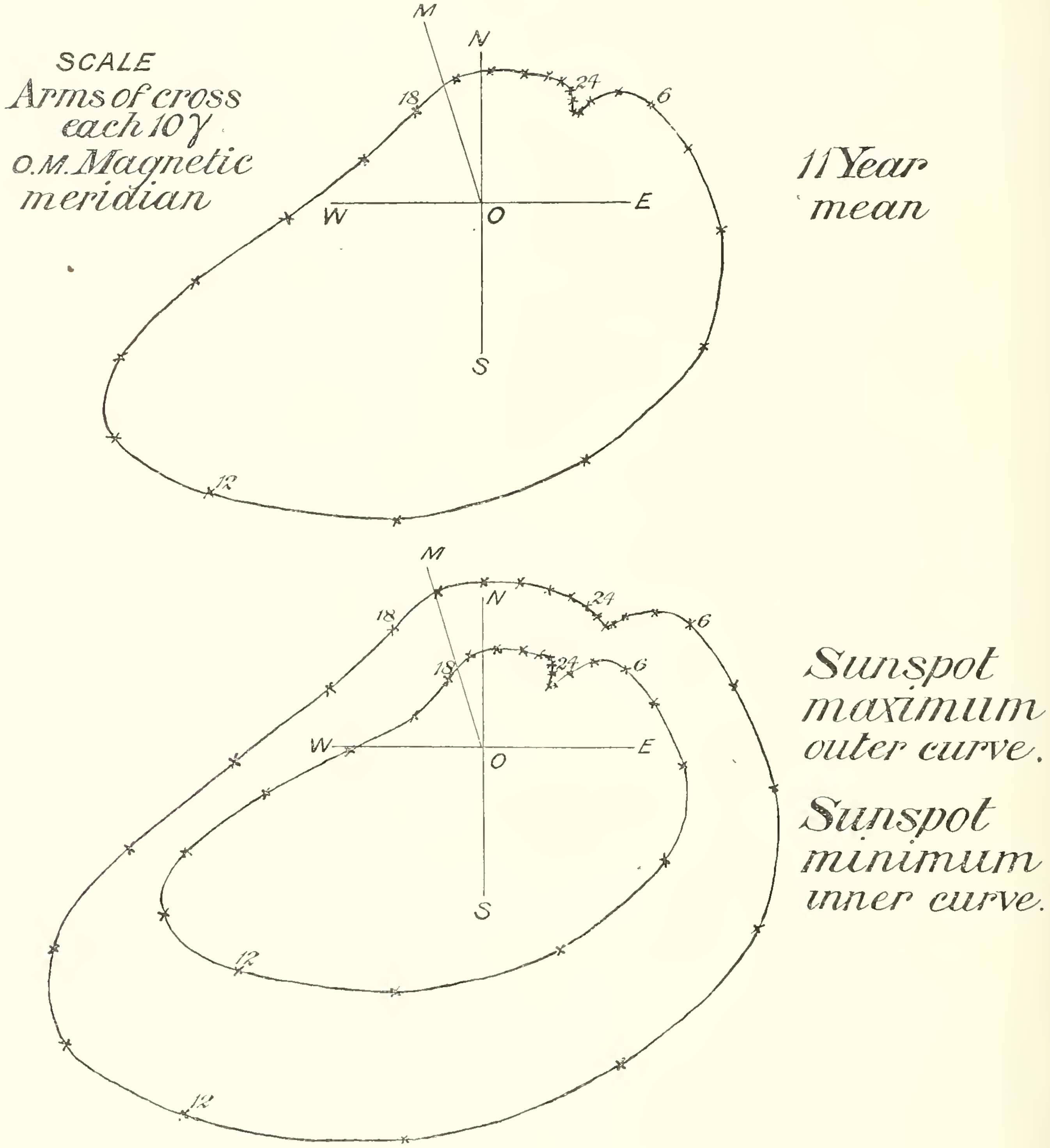

Fig. 10. Vector diagram in horizontal plane. Year.

The year diagram from the eleven years does not show a close resemblance to the diagram of any individual month in fig. 8, a suggestive fact in connection with the significance of mean diurnal inequalities for the whole year. The equinoctial months are those whose diagrams show most resemblance to that for the whole year.

§ 13. Fig. 11 shows vector diagrams in two vertical planes. The upper six curves refer to the vertical plane through the geographical west, the lower six to the vertical plane through geographical north. The upper three WV curves and the upper three NV curves represent the mean diurnal inequalities for the three seasons derived from the whole eleven years. The three lower diagrams in each case represent the mean diurnal inequality for the year, derived respectively from the sunspot minimum group of years, the whole eleven years and the sunspot maximum group of years. The origin of co-ordinates is marked in each case by a small cross. The two large crosses show the orientation, one for the WV diagrams, the other for the NV diagrams ; the arms of these crosses each represent 10γ. It will be noticed that V is measured positively downwards in both cases.

The three WV diagrams for the year differ markedly in amplitude, but comparatively little in type, closely resembling the equinoctial diagram from the eleven years. The special feature is the beak occurring about 8 a.m. This beak is also prominent in the summer diagram, occurring, however, nearly an hour earlier. Associated with the beak is an indentation or bay, extending from about 6 p.m. to 7 or 8 a.m. In the summer diagram the curvature is small near the deepest part of the bay, and except at the beak is large only from 6 to 8 p.m. In the diagrams for equinox and the year there is, as it were, a pushing forward of the shore line of the bay from 6 p.m. to midnight, leading to a marked indentation in the early morning hours. This advance of the shore line of the bay in the afternoon hours has so far developed in the winter diagram that all that remains of the bay is the very deep narrow indentation in the early morning hours. The beak is still represented in the winter diagram at 9 a.m., *i.e.*, about an hour later than in the equinoctial diagram, and two hours later than in the summer diagram, but it is now overshadowed by the protuberance near midnight.

The three NV diagrams for the whole year again differ mainly in amplitude. They all show a distinct loop near mid-day, somewhat more developed relatively in the sunspot minimum diagram than in the other two. The sunspot maximum and eleven-year diagrams show also a very small loop near 4 a.m. In the sunspot minimum diagram this is represented by a sort of tail, with its tip at 5 a.m. The hour marks for several hours on end are so nearly on a straight line, that it is impossible to say whether there is a true loop, as in the eleven-year diagram, or a very narrow indentation. The equinoctial diagram very closely resembles that for the eleven years. The summer diagram shows a considerably larger development of the mid-day loop, but the early morning loop has disappeared and is represented by a small tooth. The winter diagram shows development in an opposite direction. The mid-day loop has disappeared, and instead of a loop in the early morning there is a long narrow promontory, which like the rest of the diagram is described anti-clockwise.

A feature in NV diagrams to which attention was called some years ago by

WV vector diagrams.

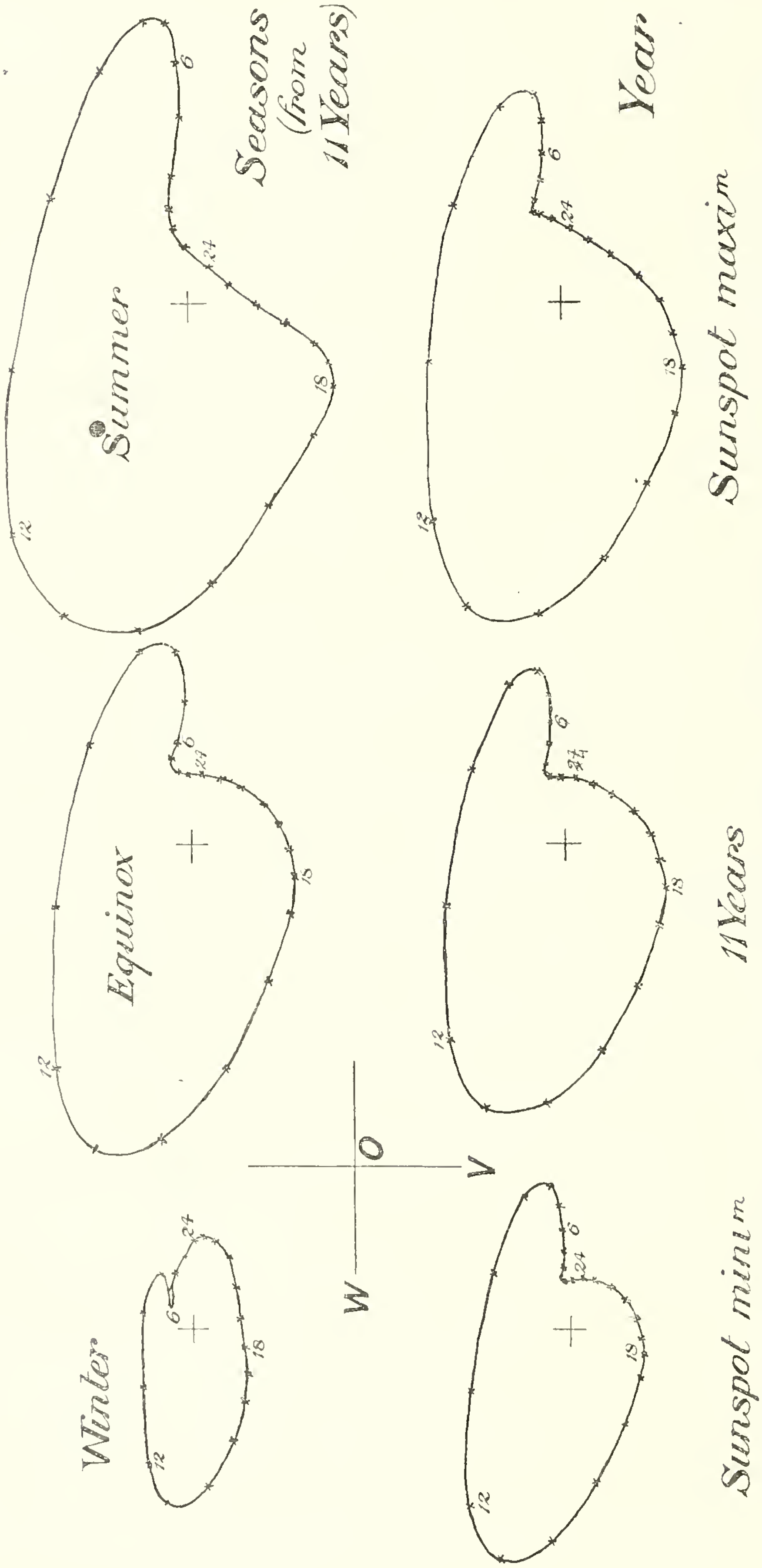

Fig. 11 (upper half). Vector diagrams in vertical plane. Small cross indicates origin of co-ordinates. Arms of large cross 10γ.

NV vector diagrams.

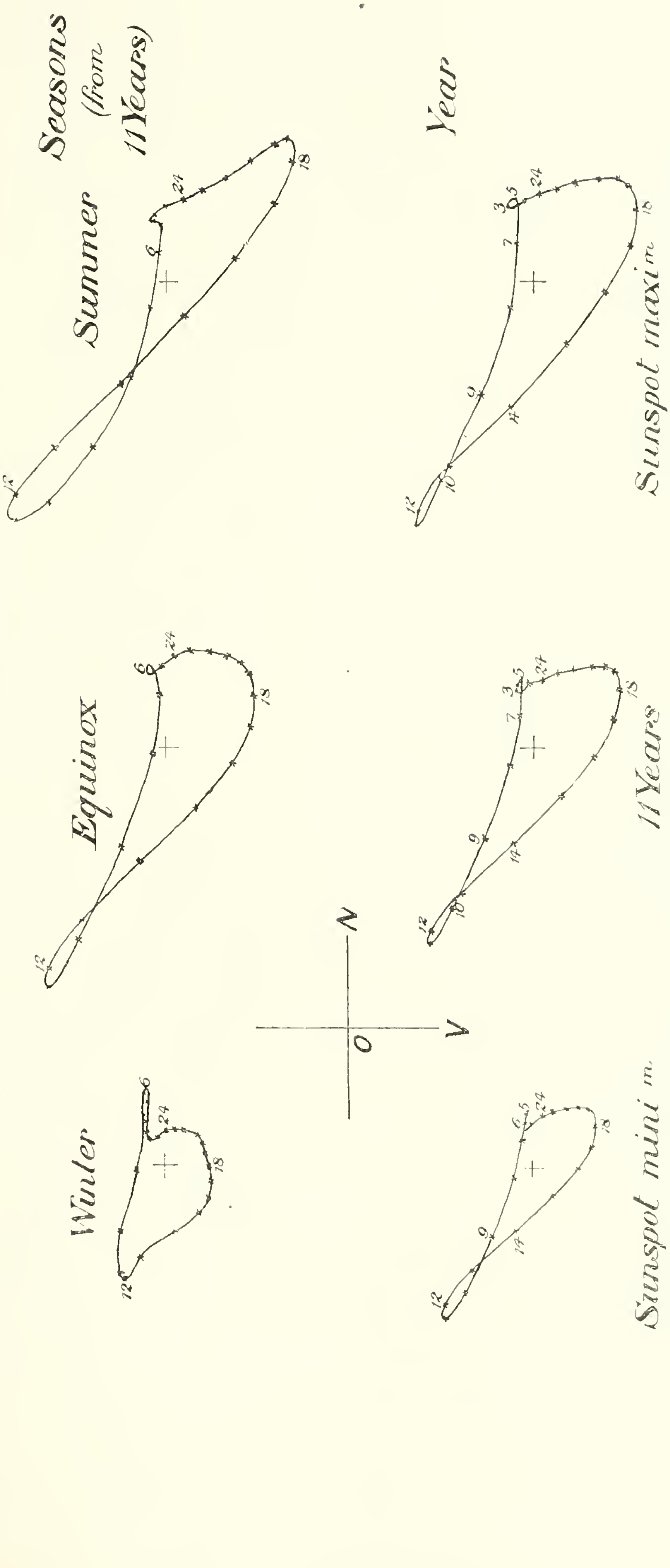

Fig. 11 (lower half). Vector diagrams in vertical plane. Small cross indicates origin of co-ordinates. Arms of large cross 10γ.

Mr. R. B. SANGSTER* is the approach which the diagram makes in the early afternoon hours to a straight line. This feature is prominent in the summer diagram between noon and 4 or 5 p.m. It is also fairly shown in the equinoctial diagram and in the diagrams for the year, especially that from sunspot maximum, but hardly in the winter diagram.

§ 14. Fig. 12 shows ordinary less quiet day difference curves, *i.e.*, the ordinate represents the algebraic excess of the ordinary day over the corresponding quiet day value in the diurnal inequality. All the curves refer to the mean diurnal inequality for the year. In the case of V, T and I there is only one curve, which corresponds to the whole eleven years. In the case of H, N and W there are three curves, representing the sunspot maximum and minimum groups of years in addition to the whole eleven years. The results were not smooth enough to justify drawing curves of continuous curvature. The scale, which is the same for all the force curves, is much more open than in the corresponding ordinary day curves.

In each case the ordinary less quiet day difference curve shows a considerable resemblance in type to the corresponding disturbed less quiet day difference curve given in a previous paper, but its amplitude is very much less.

In the case of the H difference curves in fig. 12 the amplitude is so small that a longer period than eleven years would have been needed to bring out the character fully during the night hours. There is a distinct minimum in the curve near noon—signifying that the principal daily minimum is more developed in the ordinary than in the quiet day curve—but that is perhaps the only unmistakable feature. The irregularities in the sunspot maximum and minimum curves are too great to warrant deductions as to differences between them.

The N, and still more the W, difference curves have a decidedly larger amplitude and are less irregular, especially the 11-year curves. The N difference curve has its mid-day minimum well developed, like the ordinary N curve, but it has a relatively better developed night maximum, and there seems to be no secondary maximum and minimum.

The W difference curve differs markedly from both the ordinary and quiet day curves. There is no morning minimum near 8 a.m., as in the ordinary day curve, and instead of a sharply defined maximum in the early afternoon, there is a wide plateau for some four hours on either side of noon. The largest ordinate appears at 4 p.m., *i.e.*, from two to three hours later than in the ordinary day curve. Whether the saddle near 1 p.m., which is more apparent in the sunspot maximum and minimum than in the 11-year curves, is a real or an accidental feature is open to some doubt.

The V and T difference curves closely resemble one another, as might have been inferred from the fact that the difference between ordinary and quiet day inequalities is much larger for V than for H. The two curves, while quite unlike the ordinary day V and T curves, closely resemble the disturbed less quiet day V difference

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* 'Roy. Soc. Proc.,' A, vol. 83, p. 428

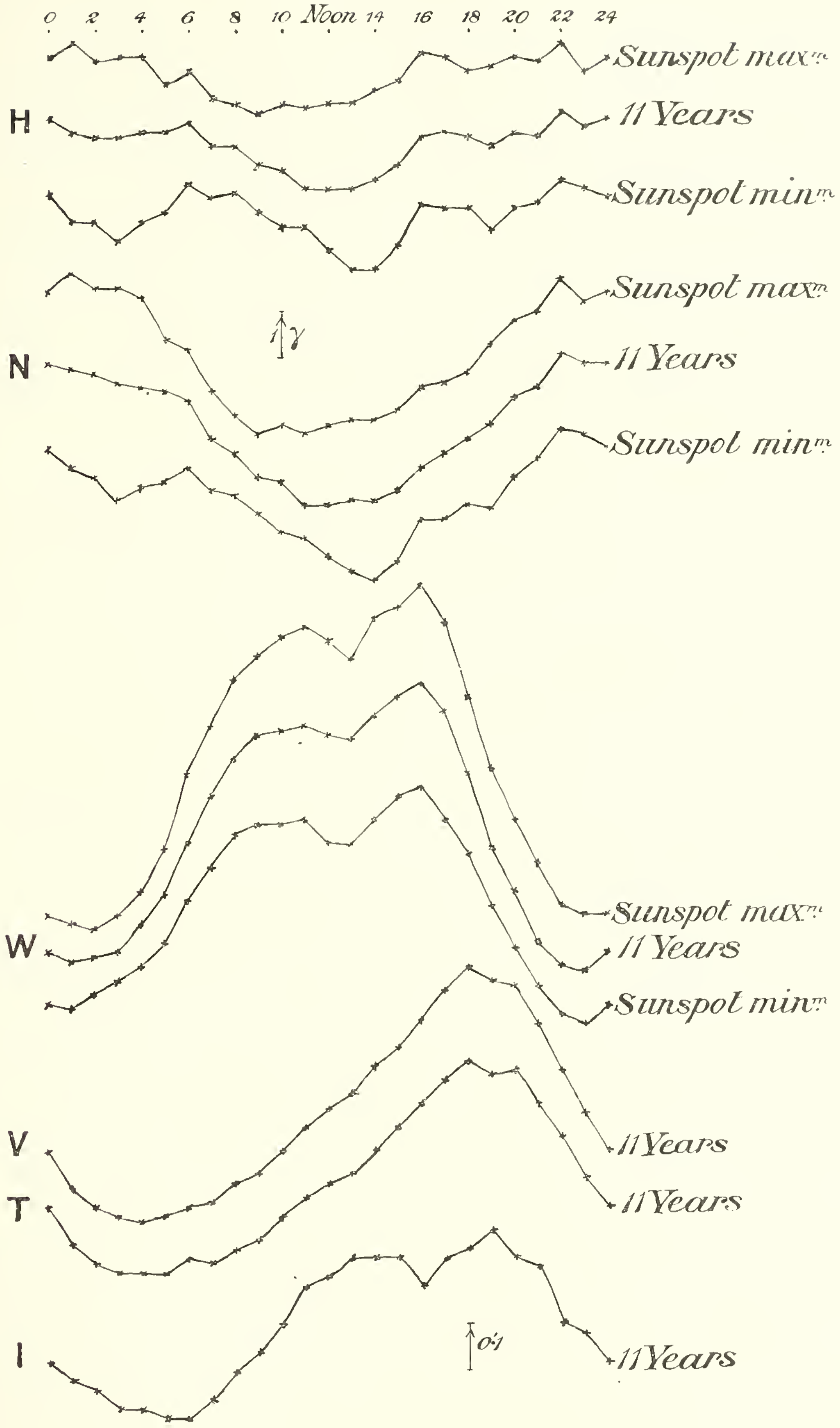

Fig. 12. Difference curves, ordinary less quiet days.

curves. They show one well marked maximum near 6 p.m., and an equally well marked minimum about 4 a.m.

The I difference curve in fig. 12 is also markedly unlike the ordinary day I curve. It has a considerable resemblance to the W difference curve, but corresponding points occur some hours later in the day in the I curve. Some doubt must be entertained as to the reality of the depression shown about 4 p.m.

The difference curves in fig. 12 indicate on the whole an increased amplitude in the ordinary day inequality as compared with that of the quiet day, but they also indicate a distinct difference in type. The nature of the difference is most conveniently considered in connection with the harmonic analysis of the inequalities. One outstanding feature has already been discussed.*

Annual Inequality.

§ 15. Let M represent the mean value of any element for the whole year, and ΔM the algebraic increment in the twelve months due to secular change, then if the secular change took place uniformly throughout the year the mean value of the element during the n^{th} month should be

$$M + (n - \tfrac{1}{2} - 6)\,\Delta M/12,$$

where n represents 1, 2, 3 up to 12.

This neglects the difference in length between different months.

If the actual mean value for the n^{th} month proves to be p_n, the values of

$$p_n - \{M + (n - \tfrac{1}{2} - 6)\,\Delta M/12\}$$

for the 12 months constitute the annual inequality.

If a magnetograph had a known and invariable base line value, the annual inequality of the corresponding element could be determined from curve readings alone. On the other hand, if an absolute instrument were invariably read when the corresponding element had its mean value for the day, the annual inequality could be got without any reference to the curves. But in practice we can tell the base line value of the curve only by reference to the absolute observations, and we cannot tell when the element had its mean value without recourse to the curves.

When base values have been assigned to all the curves, a mean value can be found for each day, representing the mean of the hourly values. From these daily means a monthly mean can be derived, representing, according to the practice of the particular observatory, the mean of all the days of the month, or the mean of all but highly disturbed days, or the mean of a limited number of selected days, *e.g.*, the 5 international quiet days. Unless all days are used, the mean of the days employed may

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* 'Roy. Soc. Proc.,' A, vol. 91, p. 370.

not fall at the centre of the month, and a question may arise as to whether some allowance should be made for this. The desirability of selecting the 5 quiet days so that their mean shall fall near the middle of the month is recognised, but such a choice is not always possible.

The practice in vogue at Kew from 1890 to 1900 was to treat the base value of each element as invariable throughout each calendar month, except in so far as it was influenced in the case of H and V by departures of the temperature of the magnetograph magnets from the mean temperature of the month. Using these base values, it would have been possible to deduce mean values depending on all the days, or on all but the highly disturbed days, in the usual way. Having regard to the special circumstances, however, a different method—presently to be described—has been adopted as equally satisfactory and much simpler. It recognises that it is really on the absolute instruments that the accuracy of the annual inequality ultimately depends. The magnetographs serve only to show what allowance has to be made to any individual absolute observation to bring it to what it would have been if taken at an hour when the element in question has its mean value for the day. To take a simple example, suppose we observed the declination daily at noon, and that in the diurnal inequality for a particular month the entry under noon is $+3'\cdot0$. Then to get the mean value of D for that particular month all we have to do is to subtract $3'\cdot0$ from the arithmetic mean of the absolute observations. The correction $-3'\cdot0$ applied to individual noon readings will not in general give exactly the mean value for the day, but so far as the monthly mean is concerned that is immaterial.

If we observe not daily but weekly, the 4 or 5 monthly days of observation at noon may all happen to depart from the average day of the month in the same direction, so that the method if applied to the observations of a single year could hardly claim to be satisfactory. If, however, we deal with the observations not of one but of a number of years, omitting days of large disturbance, accidental features must largely disappear, and this is the course that has been adopted.

The ordinary absolute observation of H consists of two parts, the vibration experiment and the deflection experiment. The mean times of these two experiments were found, and departures at each of them from the mean value for the day were deduced from the diurnal inequality, and the arithmetic mean of the two was applied with appropriate sign as a correction to the observed value of H. The inequalities, it will be remembered, were calculated for each individual month for H (and V). When the curves were considerably disturbed at the time of an absolute observation—not, of course, a frequent event—the observation was simply omitted. As highly disturbed days had also been omitted from the ordinary day diurnal inequalities, we may reasonably regard these inequalities as appropriate for the correction of the absolute observations.

It had not been the practice to commence the H observation at a fixed hour, and the time required for the deflection experiment varies somewhat according as observing conditions are more or less favourable. Still in most months the mean times of the vibration and deflection experiments fell so nearly at fixed hours that one might have applied the same correction to each observation, basing it on a mean time from all the observations. As a matter of fact, however, this simplification was not adopted when dealing with the 11 years 1890 to 1900. After 1900, as already explained, magnetic conditions were less favourable at Kew. Still electric tram disturbances are, on the whole, of a nature calculated to impair the accuracy of individual observations rather than that of the arithmetic mean of a number of observations. It thus appeared worth while investigating the annual inequality deducible from absolute observations made in years subsequent to 1900.

As corresponding diurnal inequalities from ordinary days were not available, the corrections applied to the absolute observation results to bring them to the mean value for the day were based on the inequalities of the years 1890 to 1900. In the case of H, the years 1901, 1902, 1903, 1910, 1911, 1912, and 1913, having a mean sunspot frequency of 8·8, had corrections applied from Table VII., which is based on the years 1890, 1899, and 1900, with a mean sunspot frequency of 9·6. The years 1905, 1906, and 1907, having a mean sunspot frequency of 59·9, had corrections applied from Table VI., which is based on the years 1892 to 1895, with a mean sunspot frequency of 75·0. The two years 1904 and 1909, having sunspot frequencies of 42·0 and 43·9 respectively, had corrections applied from Table V. for the 11 years 1890 to 1900, with a mean sunspot frequency of 41·7. The year 1908 was omitted, because the deflection distances were increased from two to three at midsummer, and this possibly might have introduced some discontinuity. The final outcome was that the twelve years dealt with had corrections applied as if their mean sunspot frequency were 31, whereas it was really 27. As we shall see later, the amplitude of the diurnal inequality in H and the sunspot frequency are connected, at least approximately, by a linear relationship. Extrapolation from one period of years to another is of course always a matter of some uncertainty; still there is considerable ground for believing that the accuracy of the inequality derived from the second period of years is not greatly inferior to that derived from the first.

In the case of I the observation had been taken almost invariably in the afternoon, the mean time of observation falling within 30 minutes of 3 p.m. Near this hour I changes slowly, and its departure from the mean value for the day is not large. To have got out diurnal inequalities of I for each month of the 11 years would have entailed an immense amount of labour. Thus corrections to the observed values were simply derived from the mean inequalities from the 11 years given in Table XIV., and the corrections were calculated for the mean time of all the observations of the month, not for the times of the individual observations, unless these times varied more than was generally the case. The I observational data from the 14 years 1901 to 1914 were similarly treated, use being again made of the diurnal inequalities in Table XIV.

§ 16 Values having been obtained from the absolute observations of each month corrected for diurnal variation, the means for all the months of the same name were summed and meaned, the 11-year period and the later period being treated separately. The monthly means thus obtained represented the average annual change from mid-January to mid-December, comprising the annual inequality and the secular change. It remained to eliminate the secular change.

In the case of the 11-year period, the mean annual secular change of H between 1890·5 and 1900·5 derived from the quiet days was $+25{\cdot}9\gamma$. A small difference has been observed at several stations between mean annual values of H derived respectively from quiet days and from all or all ordinary days, the former mean exceeding the latter. The difference, however, is only of the order 3γ, and as 1890 and 1900 were both quiet years of very similar character, any uncertainty of this kind spread over a 10-year period must have been negligible. A confirmation of the accuracy of the quiet day estimate was derived by taking arithmetic means for 1890 and 1900 of the twelve monthly means of the absolute observations, corrected for diurnal variation. The mean thus obtained for 1900 exceeded that obtained for 1890 by $259{\cdot}5\gamma$, giving $+25{\cdot}9_5$ for the mean secular change.

In the case of the second group of years, the mean secular change in H—as obtained from the annually published quiet day results, allowing for changes of constants and procedure—was only $+5{\cdot}8_2\gamma$. In the case of I the mean secular changes accepted were $-2'{\cdot}25_5$ for the first period and $-1'{\cdot}05_5$ for the second.

The substitution of these respective values for ΔM in the formula in § 15 led to the annual inequalities for H and I given in Table XVIII. The annual inequalities given for V in that table were calculated from the formula expressing changes in V in terms of changes in H and I, employing mean values for the numerical coefficients of ΔH and ΔI. At the foot means are given for the ordinary three seasons. The centre of each season falls at the middle of the year, so these seasonal values are unaffected by the secular change, or by any error that may have been made in estimating its amount.

The greater or less smoothness of the inequalities, and the amount of accordance between the results from the two periods, are the chief criteria for estimating the reliability of the data in Table XVIII. Both criteria are less favourable towards the inequality in V than towards those in H and I. The V inequality from the 11-year period is very irregular, plus and minus signs occurring rather promiscuously; and while the corresponding seasonal means from the two periods agree in sign, the winter and summer means from the second period are numerically much larger than those from the first. The lesser consistency of the V inequality is hardly surprising since it suffers from every uncertainty or accident that affects either the H or the I inequality. A change of 10γ in H alters I as much as a change of 24γ in V. Thus the deduction of changes in V from the combination of observed changes in I and H, though the only way feasible, does not promise high accuracy.

There is a regularity in both sets of figures for H which can hardly be accidental. They agree in making the successive monthly values all positive from May to August, and all negative from September to February. Both periods show a clear maximum in the summer months, but one puts the minimum in winter, the other in equinox. The inequality obtained by combining the two periods, allowing them equal weights, makes the winter and equinoctial values practically equal. It shows a range of 12·5γ, the maximum coming in June, and the minimum in November.

TABLE XVIII.—Annual Inequality.

Month and season.	Horizontal force.			Inclination.			Vertical force.		
	First period.	Second period.	Mean.	First period.	Second period.	Mean.	First period.	Second period.	Mean.
	γ	γ	γ	′	′	′	γ	γ	γ
January . . .	−2·0	−1·8	−1·9	+0·19	0·00	+0·09	+1·9	− 4·4	−1·2
February . . .	−0·1	−1·6	−0·9	+0·03	+0·06	+0·04	+0·8	− 1·8	−0·5
March.	−4·5	+3·5	−0·5	+0·41	−0·07	+0·17	+4·1	+ 6·0	+5·0
April	−2·3	+0·5	−0·9	+0·08	+0·09	+0·08	−2·6	+ 4·4	+0·9
May.	+3·1	+5·6	+4·3	−0·08	−0·17	−0·12	+4·7	+ 7·3	+6·0
June	+8·8	+7·0	+7·9	−0·56	−0·16	−0·36	+1·0	+10·9	+5·9
July	+2·6	+2·3	+2·5	−0·26	−0·18	−0·22	−3·0	− 0·8	−1·9
August	+4·4	+0·5	+2·5	−0·23	−0·07	−0·15	+2·2	− 1·3	+0·4
September . .	−4·2	−2·7	−3·4	+0·12	−0·06	+0·03	−5·6	− 8·5	−7·1
October	−3·4	−3·7	−3·6	+0·25	+0·14	+0·19	+0·8	− 4·0	−1·6
November. . .	−1·9	−7·3	−4·6	+0·21	+0·36	+0·29	+3·0	− 4·4	−0·7
December. . .	−0·9	−1·7	−1·3	−0·16	+0·06	−0·05	−8·0	− 2·2	−5·1
Winter	−1·2	−3·1	−2·2	+0·07	+0·12	+0·09	−0·6	− 3·2	−1·9
Equinox. . . .	−3·6	−0·6	−2·1	+0·22	+0·03	+0·12	−0·8	− 0·5	−0·7
Summer. . . .	+4·7	+3·8	+4·3	−0·28	−0·14	−0·21	+1·2	+ 4·0	+2·6

In the case of I the two periods agree in showing a distinct minimum in summer, but the one places the maximum in winter, the other in equinox. Combining the two periods, allowing them equal weight, we get a comparatively smooth inequality with a range of 0′·65, the maximum coming in November, the minimum in June. The type is on the whole fairly similar to that of results that have been published for Parc St. Maur and Potsdam, and for the northern hemisphere as a whole by LIZNAR and HANN, but the range shown in Table XVIII. is a good deal less than in the cases quoted.

Assuming that the phenomena are not of instrumental origin, it seems reasonably certain, after allowing for a secular change progressing at a uniform rate throughout the year, that H is higher and I lower in summer than in winter. Also it seems probable, though more open to doubt, that V displays the same phenomena as H. This agrees with the results obtained from quiet days alone in a previous paper.

§ 17. The possibility that the phenomena owe something to instrumental causes must be recognised. If there is any instrumental cause at work, it is presumably of thermal origin. In the case of I, any sensible temperature effect on the absolute observations is difficult to imagine. The strength of the dip needles, it is true, may not be the same, when they are stroked at 25° C. as when they are stroked at 10° C. I have no statistics on the subject. Also the distance of the centre of gravity from the axis of suspension will naturally increase with rise of temperature. Thus there would be nothing very surprising if the inclination observed with one particular end of the needle dipping varied slightly with temperature. But the reversal of the poles, invariably observed at Kew, ought to eliminate this as a first approximation, leaving only second order terms, which one would not expect to be sensible. The absolute observation hut at Kew is heated by a lamp in cold weather, so that the difference between summer and winter temperatures of observation is only of the order of 10° C. For the diurnal inequality in I we are dependent on the H and V magnetographs, the latter of which has a large temperature coefficient. An error in the value accepted for that coefficient, or in the results accepted for the diurnal variation of temperature of the V magnet, might introduce a differential error as between summer and winter. Any such error would affect the accuracy of the corrections applied to the observed inclinations to reduce them to the mean value for the day. The hour at which the observations is taken is, however, one at which the change is not rapid either in the inclination or in the temperature of the magnetograph room. Thus any considerable error seems improbable.

§ 18. In the case of H, the ways in which temperature might come in are more numerous. There might be an error in the temperature coefficient of the collimator magnet, but the consequences of this would not be nearly so serious as might appear at first sight. What really concerns us in this connection is not the mean temperature of the whole H observation, but only the difference between the temperatures in the vibration and deflection experiments, which is usually only 1° or 2° C. In the present case, moreover, the error would come in not on the average size of this difference, but only on its seasonal variation. Temperature practically always rises during an H observation, and so is higher during the deflection experiment, which comes last, than during the vibration experiment. If there were no artificial heating the difference would naturally be greatest in summer, so a seasonal differential error is conceivable. If it existed, however, it should show itself in an apparent seasonal variation in the values found for the magnetic moment of the collimator magnet reduced to 0° C., and a special investigation showed no trace of this.

Errors in the values assumed for the variation with temperature of the length of the deflection bar and the moment of inertia of the collimator magnet would come in on the full annual range of temperature in the magnetic hut, but coefficients of thermal expansion in brass and steel are small quantities, and any large percentage error in them is most improbable. The temperature coefficient of the H magnetograph is small, and the general accordance of individual H observations and curve measurements seems to preclude the possibility of any large percentage error in the value accepted.

There is, in short, no direct evidence of the existence of uncorrected temperature effects, while there is a good deal in favour of the substantial accuracy of the allowances made. At the same time, direct experiment, if possible without undue risk of interfering with the records, would be desirable.

Fourier Coefficients.

§ 19. The analysis of the diurnal inequalities into series of harmonic terms whose periods are 24, 12, &c., hours is part of the regular routine at some observatories. To some people circular functions seem on a wholly superior plane to all others, and the analysis of diurnal inequalities according to any other type of function would appear almost inconceivable. Others may argue that the employment of circular functions for the representation of magnetic diurnal inequalities may hide rather than reveal what is of real physical importance. There are several common-sense arguments in favour of the analysis in series of sines and cosines. The use of these is so very general that for the intercomparison of results at different stations there is really no competing series. Again, it is found that as a rule 4 Fourier waves—*i.e.*, terms with periods of 24, 12, 8 and 6 hours—suffice to give a very close approximation to the observed diurnal inequality, and the 8-hour and 6-hour waves are usually small compared with the first two. There is thus a good deal to be said for the argument that the Fourier analysis is a natural one. This argument of course would lose much of its force if a single function of the time, of a not unduly complicated form, with only 2 or 3 parameters sufficed to represent the diurnal inequality adequately at a number of stations. But until such a function has been proved to exist, the course which is followed here of employing ordinary Fourier series is likely to commend itself to the majority.

The diurnal inequality is usually expressed in one of the alternative forms

$$a_1 \cos t + b_1 \sin t + a_2 \cos 2t + b_2 \sin 2t + \dots$$
$$c_1 \sin (t+\alpha_1) + c_2 \sin (2t+\alpha_2) + \dots ,$$

where t represents time counted from midnight, one hour in t being taken as the equivalent of 15°. The constants a, b of the first series, or c, α of the second, are generally called Fourier coefficients, c representing the amplitude and α the phase angle. The usual process is to calculate the a, b constants from the hourly values in the diurnal inequality, and then deduce the c, α constants from the equations

$$\tan \alpha = a/b, \quad c \equiv \sqrt{a^2+b^2} = a/\sin \alpha = b/\cos \alpha.$$

If a, b coefficients have been calculated for three magnetic elements, they can be deduced at once for any other element, through the formula expressing it in terms of the first three. Thus it sufficed to calculate the *a*, *b* coefficients in the usual way for D, H and V, and the work so far as D is concerned had been already done.

The values of *a* and *b* for the year, or for any season, are the arithmetic means of the values from the included months. They can thus be deduced at pleasure from the values of *a* and *b* calculated for the included months, or be specially calculated from the inequality for the season. The employment of both methods puts the accuracy of the calculations to a very severe test. In fact, to secure agreement to say three significant figures it is necessary to carry the calculation at least one place further. This test was not in general applied, but all the calculations were carefully checked, special attention being given to any apparent irregularities.

Table XIX.—Horizontal Force (Local Mean Time for Phase Angles).

Year.	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
	γ.	°	γ.	°	γ.	°	γ.	°
1890	6·81	119·2	4·01	312·4	2·18	175	1·13	28
1891	9·66	117·1	5·62	303·7	2·37	166	1·02	23
1892	13·00	117·2	6·52	301·6	2·81	166	1·32	22
1893	13·35	114·1	7·45	301·7	3·26	163	1·33	18
1894	13·26	113·9	7·09	294·9	2·60	167	1·26	24
1895	11·73	113·3	6·15	298·9	2·57	171	1·20	22
1896	9·81	114·8	5·22	297·2	2·48	166	1·24	17
1897	8·56	112·3	4·61	294·8	1·99	173	1·30	28
1898	8·36	115·9	4·14	302·1	2·17	166	1·04	25
1899	8·10	115·8	4·09	302·5	2·36	174	1·10	32
1900	6·56	119·0	3·85	306·7	2·16	178	1·12	20

Tables XIX. and XX. give the amplitudes and phase angles for the 24-, 12-, 8- and 6-hour terms in the H and V mean diurnal inequalities for the whole year, each of the eleven years being treated separately.

Table XX.—Vertical Force (Local Mean Time for Phase Angles).

Year.	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
	γ.	°	γ.	°	γ.	°	γ.	°
1890	5·08	139·4	3·39	273·3	1·36	106	0·47	282
1891	6·84	145·1	4·79	272·1	1·64	96	0·60	295
1892	8·10	148·8	5·29	268·5	1·77	101	0·69	280
1893	7·26	138·8	5·62	270·1	2·26	97	0·71	279
1894	8·38	145·8	5·32	269·0	2·02	95	0·60	292
1895	7·70	148·1	5·09	271·6	1·83	97	0·68	295
1896	7·54	143·5	4·60	270·6	1·78	105	0·61	284
1897	7·07	138·5	3·95	268·6	1·48	101	0·52	286
1898	6·95	142·7	4·25	274·2	1·50	108	0·49	286
1899	6·00	144·0	3·87	271·3	1·31	107	0·52	284
1900	5·38	130·0	3·48	276·1	1·60	103	0·61	281

G.M.T. was employed, as already stated, in the diurnal inequalities, and thus the values deduced in the first instance for the Fourier coefficients referred to G.M.T. Local mean time is, however, more generally instructive, and accordingly the necessary transference to local time has been made in Tables XIX. and XX., and all the subsequent tables relating to Fourier coefficients. The transference does not affect the amplitudes. The corrections it requires to the phase angles are

$$+19' \text{ in } \alpha_1, \ +38' \text{ in } \alpha_2, \ +57' \text{ in } \alpha_3 \text{ and } +1^\circ\ 16' \text{ in } \alpha_4,$$

Kew local time being the equivalent of 19′ after Greenwich.

The relation with sunspots will be discussed more fully later, but the significance of the tables will be better understood if regard is paid to the following facts. 1890 was a year of sunspot minimum with a frequency of 7·1. The frequency rose rapidly to a maximum of 84·9 in 1893, and fell more slowly to 9·5 in 1900. In 1898 there was a slight arrest in the fall, the mean frequency being 26·7 as compared with 26·2 in 1897. The year 1893, though the year of sunspot maximum, was on the whole a quiet year free from large disturbances, much quieter than 1892, 1894 or 1895.

In Table XIX. c_1, c_2, c_3 and c_4 all rise to a maximum in 1893, and the general parallelism with the sunspot variation is readily seen, especially in c_1 and c_2. Table XX. shows a similar state of matters, except that the value of c_1 in 1893 fell short of that in several adjacent years.

The variation in the phase angle is by no means so decisive. In Table XIX. the largest values of α_1 and α_2 are associated with the years of sunspot minimum, but the smallest values occur in 1897, an intermediate year as regards sunspots. Accident seems to play a sensible part in the relation between phase angles in successive years, especially in the case of α_3 and α_4. The same remark applies in even greater measure to Table XX.

In fact the influence of sunspot frequency on the phase is so small that for its study it is desirable to combine the years in groups representative respectively of large and small sunspot frequency, in hopes of eliminating accidental features.

§ 20. Tables XXI. and XXII. show the variation in amplitude and phase angle throughout the year in the Fourier waves representing the diurnal inequality in H, and Tables XXIII. and XXIV. do the same for V. Results are given for the whole 11 years, also for 1890, 1899 and 1900 representing few sunspots, and 1892 to 1895 representing many sunspots. Arithmetic means from the 12 months are given in Tables XXI. and XXIII. When there is considerable variation of phase throughout the year, contributions from different months to the seasonal and yearly diurnal inequalities to some extent neutralise one another. Thus frequently a better idea of the average activity of the forces to which any particular Fourier wave is due is derivable from the arithmetic mean of the c's than from the corresponding c in the mean diurnal inequality for the year.

TABLE XXI.—Horizontal Force. (Unit 1γ.)

Month.	c_1.			c_2.			c_3.			c_4.		
	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.
January . . .	1·23	3·15	5·41	1·80	3·41	4·46	2·27	2·26	2·52	1·16	1·29	1·33
February. . .	2·93	4·50	6·33	2·46	3·54	5·02	2·45	2·68	3·14	1·31	1·26	1·18
March	6·55	9·13	11·78	4·31	5·66	7·46	3·39	3·75	4·53	1·44	1·63	1·88
April.	10·27	14·43	18·44	5·37	7·55	9·20	3·17	3·61	4·17	1·32	1·65	2·09
May	12·21	15·83	19·14	4·94	6·44	8·11	1·32	1·25	1·57	0·86	1·04	1·18
June	13·18	17·18	21·56	5·58	7·06	9·26	1·85	1·73	2·45	0·88	0·71	0·96
July	12·94	17·17	21·86	4·83	7·06	9·10	2·36	2·01	1·99	0·95	0·73	0·88
August. . . .	12·41	15·97	19·70	4·74	6·35	7·90	3·12	3·18	3·44	1·40	1·43	1·32
September . .	10·60	13·17	15·31	5·05	5·71	6·33	3·63	3·84	3·96	1·84	1·88	1·97
October . . .	8·03	10·89	13·88	4·88	6·14	8·02	2·72	3·66	4·30	1·13	1·62	1·91
November . .	3·05	5·20	7·98	3·72	4·54	5·68	1·85	2·21	2·61	0·92	1·13	1·18
December . .	2·66	3·30	4·73	2·59	3·32	4·25	1·53	1·62	2·07	0·67	0·57	0·46
Arithmetic means .	8·01	10·83	13·84	4·19	5·56	7·07	2·47	2·65	3·06	1·16	1·25	1·36

In the case of c_1 and c_2, whether in Table XXI. or Table XXIII., there is no single month in which the amplitude fails to show an increase as we pass from the sunspot minimum to the sunspot maximum group of years. In the case of c_3 and c_4 the same is generally true, but there are a few exceptions, presumably accidental in both tables.

TABLE XXII.—Horizontal Force. Phase Angles referred to Local Mean Time.

Month.	a_1.			a_2.			a_3			a_4.		
	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.
	° ′	° ′	° ′	° ′	° ′	° ′	°	°	°	°	°	°
January	−24 24	51 43	67 12	298 41	282 8	279 30	167·5	157·9	152·1	8·5	3·5	−2·7
February.	69 21	70 49	77 46	280 32	269 56	271 57	146·7	146·3	141·2	−9·4	−5·2	5·9
March	103 28	101 8	102 29	297 55	294 15	295 28	154·0	153·5	153·6	0·4	−1·4	−6·2
April	115 32	114 51	115 30	299 0	297 51	297 45	145·3	150·1	152·3	13·1	20·4	20·3
May	132 15	131 27	130 17	317 28	307 52	302 44	217·0	204·5	198·5	59·9	67·0	63·3
June	131 37	134 43	136 25	306 54	308 24	312 5	200·8	213·3	216·0	37·0	53·3	67·2
July	134 16	134 5	134 20	321 2	310 37	307 59	204·5	191·9	179·9	42·1	30·1	30·8
August	129 21	127 58	126 44	338 46	327 27	322 17	212·4	203·8	197·8	32·2	33·9	24·7
September	116 18	113 58	111 58	320 32	320 48	318 10	187·8	188·3	183·7	34·6	33·5	38·0
October	94 47	94 30	93 43	294 57	295 57	297 8	162·8	162·9	160·8	25·4	21·3	16·2
November	80 37	76 20	77 37	289 21	282 28	279 45	158·9	153·9	149·1	40·7	24·0	6·8
December	13 50	37 45	54 31	280 16	268 59	265 50	145·6	141·8	134·2	34·3	15·8	4·4

The annual variation in the amplitude is clearly shown in all cases, but it follows different laws in the different waves. c_1 and c_2 in both H and V have a well marked minimum near midwinter and a maximum near midsummer. c_3 and c_4 also exhibit a minimum near midwinter, but there is a second minimum—which in the case of c_3 in Table XXI. is actually the principal minimum—near midsummer. The largest values in c_3 and c_4 present themselves in equinoctial months.

TABLE XXIII.—Vertical Force. (Unit 1γ.)

Month.	c_1.			c_2.			c_3.			c_4.		
	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.
January . . .	2·72	3·53	4·39	1·10	1·32	1·70	0·51	0·57	0·71	0·28	0·44	0·54
February. . .	3·88	5·01	5·98	1·94	2·72	3·29	1·03	1·31	1·58	0·36	0·47	0·63
March	5·70	7·03	7·26	4·21	5·37	6·24	2·17	2·44	2·78	0·94	0·98	1·04
April.	7·81	8·39	8·50	5·38	6·49	7·47	2·24	2·75	3·03	0·70	0·82	0·87
May	9·28	10·88	12·18	6·02	7·62	9·26	1·93	2·10	2·25	0·52	0·63	0·60
June	8·49	10·33	11·49	5·28	6·65	8·22	1·27	1·42	1·80	0·47	0·36	0·32
July	8·76	11·07	13·54	5·12	6·38	7·55	1·40	1·66	2·01	0·43	0·37	0·37
August. . . .	5·61	7.37	7·78	5·27	6·21	6·75	2·05	2·47	2·89	0·62	0·62	0·64
September . .	5·89	7·64	8·35	3·90	4·86	5·34	1·96	2·07	2·25	0·85	0·81	0·91
October . . .	3·90	5·78	7·27	2·07	3·49	4·17	1·59	1·89	2·29	0·86	1·04	1·18
November . .	3·08	4·47	5·32	1·61	2·11	2·64	0·74	1·00	1·32	0·61	0·68	0·80
December . .	1·79	2·95	4·02	0·88	1·26	1·78	0·53	0·78	1·06	0·10	0·21	0·41
Arithmetic means .	5·58	7·04	8·01	3·56	4·54	5·37	1·45	1·70	2·00	0·56	0·62	0·69

TABLE XXIV.—Vertical Force. Phase Angles referred to Local Mean Time.

Month.	α_1.			α_2.			α_3.			α_4.		
	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.	S. minimum.	11 years.	S. maximum.
	°	°	°	°	°	°	°	°	°	°	°	°
January . . .	164·1	160·8	157·9	287·9	283·4	275·0	145	118	101	267	277	281
February . .	154·6	155·7	154·5	269·8	275·9	278·1	104	100	98	237	261	282
March	133·3	143·9	150·3	272·7	270·7	268·6	94	93	87	268	275	282
April.	121·8	130·5	132·1	265·4	263·3	260·3	95	94	92	293	300	298
May	126·9	129·3	129·5	274·9	270·3	268·4	103	102	99	302	314	327
June	136·2	139·5	140·9	271·2	268·9	268·3	107	100	98	307	315	307
July	145·2	142·8	146·3	266·3	263·6	262·7	91	82	78	260	245	219
August. . . .	128·8	134·5	136·3	276·8	273·5	273·5	104	102	101	285	280	281
September . .	139·4	143·1	145·3	279·4	276·6	277·7	116	109	108	290	297	298
October . . .	141·7	149·5	153·6	267·2	269·5	267·6	102	102	95	281	287	284
November . .	170·4	171·8	174·6	308·7	297·1	292·5	138	125	108	302	286	278
December . .	143·0	155·9	163·7	281·2	274·3	269·4	125	119	120	306	267	269

In the case of the phase angles the difference between sunspot maximum and minimum years is much less decisive. α_3 in V in every month of the year is larger—*i.e.*, speaking generally, the maximum occurs earlier in the day—in sunspot minimum than in sunspot maximum. There is also a large preponderance of months in which the sunspot minimum angle is the larger in the cases of α_3 in H and of α_2 in both H and V. α_1, however, in V shows exactly the opposite phenomenon, while α_1 in H and α_4 in both H and V show no decided tendency.

In H all four phase angles exhibit the same tendency in their annual variation. They are distinctly larger in summer than in winter. This is especially conspicuous in the case of α_1; in sunspot minimum the phases of the 24-hour term in January and July approach opposition.

An increase in phase angle means in a general sense an earlier occurrence in the maximum and minimum, but this requires special interpretation at times. Take, for instance, the 11-year values of α_1 in H. In January and February the values are respectively 51° 43′ and 70° 49′. The corresponding times of occurrence of the maximum are respectively

$$\text{In January } t = (90-51\cdot72)/15 = 28\cdot28/15 = 1\cdot89 \text{ hour} = 1 \text{ hour } 53 \text{ minutes.}$$

$$\text{In February } t = (90-70\cdot82)/15 = 19\cdot18/15 = 1\cdot28 \text{ hour} = 1 \text{ hour } 17 \text{ minutes.}$$

But when we pass to March the phase angle 101° 8′ falls in a different quadrant, and the time of the maximum is given by

$$t = (450-101\cdot13)/15 = 23\cdot3 \text{ hour} = 23 \text{ hours } 18 \text{ minutes.}$$

In a sense the maximum has become earlier in March, only it has as it were transferred itself to the previous day; the wave, in fact had already passed its maximum when the day commenced. The minima in the three months occur in January at 13 hours 53 minutes, in February at 13 hours 17 minutes, and in March at 11 hours 18 minutes. Thus the statement that the minimum has become earlier as the phase angle increased was in this case literally true.

In the case of V in Table XXIV. the annual change is on the whole in the opposite direction to that in H, the angles α_1, α_2 and α_3 being all smaller in summer than in winter. There seems to be a very appreciable accidental element in the values obtained for individual months, especially in the case of α_4.

The mode of annual variation of the amplitudes of the several Fourier waves is best shown by expressing the values for different months as fractions of their arithmetic mean. This has been done for the full 11-year results in Table XXV., data being given for both H and V. The laws of annual variation for the two elements proved sufficiently alike to encourage the formation of the arithmetic means from the two. These arithmetic means are considerably smoother than the data from H or V alone.

Relatively considered, the amplitudes of the first four Fourier waves show a fairly similar range of annual variation. On the whole the range is largest in c_1 and least in c_3; but c_3 and c_4, having a double annual period, vary most rapidly.

TABLE XXV.—Ratios to Arithmetic Mean (11 years' data).

Month.	c_1.			c_2.			c_3.			c_4.		
	H.	V.	Mean.	H.	V.	Mean.	H.	V.	Mean.	H.	V.	Mean.
January . . .	0·29	0·50	0·40	0·61	0·29	0·45	0·85	0·33	0·59	1·03	0·72	0·87
February . .	0·42	0·71	0·56	0·64	0·60	0·62	1·01	0·77	0·89	1·01	0·75	0·88
March	0·84	1·00	0·92	1·02	1·18	1·10	1·41	1·43	1·42	1·31	1·58	1·45
April.	1·33	1·19	1·26	1·36	1·43	1·39	1·36	1·61	1·49	1·32	1·32	1·32
May	1·46	1·55	1·50	1·16	1·68	1·42	0·47	1·23	0·85	0·83	1·02	0·93
June	1·59	1·47	1·53	1·27	1·46	1·37	0·65	0·83	0·74	0·57	0·58	0·57
July	1·59	1·57	1·58	1·27	1·41	1·34	0·76	0·97	0·87	0·59	0·60	0·59
August . . .	1·48	1·05	1·26	1·14	1·37	1·25	1·20	1·45	1·32	1·15	1·00	1·08
September . .	1·22	1·09	1·15	1·03	1·07	1·05	1·45	1·21	1·33	1·51	1·31	1·41
October . . .	1·01	0·82	0·91	1·10	0·77	0·94	1·38	1·11	1·25	1·30	1·68	1·49
November . .	0·48	0·64	0·56	0·82	0·46	0·64	0·84	0·58	0·71	0·91	1·10	1·01
December . .	0·30	0·42	0·36	0·60	0·28	0·44	0·61	0·46	0·53	0·46	0·34	0·40

§ 21. Fourier coefficients were not calculated for the individual months of the year except for H and V. For the other elements they were calculated only for the diurnal inequalities from the seasons and the year. Table XXVI. compares the amplitudes in these seasonal diurnal variations for H, V, T, N, W, and I, use being made in dealing with N and W of the results previously obtained for D. In the case of c_1 and c_2 the equinoctial value is always intermediate in size between the winter and summer values, and somewhat in excess of the value for the whole year. In the case of c_3 and c_4 the equinoctial value is invariably in excess of both the winter and summer values, and much in excess of the value for the year. In the case of c_3 the summer value is the lowest for two elements, N and H; in the case of c_4 the winter value is less than the summer value in no element except I.

In the case of all the Fourier waves for the three rectangular components V, N, and W, the year value of the amplitude is largest in W and least in V. This is in general true also of the three seasonal values, but in equinox c_1 is larger in N than in W, and there are one or two cases in which the V value is not the lowest.

Table XXVII. shows the ratios borne by the amplitudes of the 12-, 8-, and 6-hour waves to the amplitude of the corresponding 24-hour wave. In the case of H, T, N, and I, the importance of the 12-, 8-, and 6-hour waves falls relative to that of the 24-hour wave as we pass from winter to equinox, and from equinox to summer; but in W and V the relative importance of the shorter period waves is greatest in equinox, and in the case of the 12-hour wave it is least in winter.

TABLE XXVI.—Amplitudes of Fourier Waves (11 years' data). (Unit 1γ in Force Components.)

Element.	c_1.				c_2.				c_3.				c_4.			
	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
H	9·94	3·90	11·77	16·52	5·34	3·68	6·02	6·66	2·44	2·18	3·59	2·03	1·18	1·04	1·66	0·95
V	6·91	3·96	7·16	9·87	4·51	1·83	5·03	6·70	1·68	0·90	2·27	1·89	0·59	0·44	0·90	0·44
T	9·92	3·72	10·67	15·44	6·02	3·09	6·76	8·22	2·08	1·58	2·95	1·71	0·67	0·56	1·04	0·42
N	12·11	6·76	14·66	16·51	6·31	4·29	7·16	7·79	2·18	2·25	3·21	1·19	0·82	0·77	1·18	0·73
W	13·43	8·65	13·95	19·52	8·76	4·60	10·11	11·94	4·30	2·36	5·80	4·83	1·64	1·60	2·49	0·84
I	0'·500	0'·298	0'·629	0'·829	0'·255	0'·195	0'·302	0'·337	0'·153	0'·126	0'·220	0'·158	0'·082	0'·071	0'·113	0'·077

TABLE XXVII.—Ratios of Amplitudes of Fourier Waves (11 years' data).

Element.	c_2/c_1.				c_3/c_1.				c_4/c_1.			
	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
H	0·54	0·94	0·52	0·40	0·25	0·56	0·30	0·12	0·12	0·27	0·14	0·06
V	0·65	0·46	0·70	0·68	0·24	0·23	0·32	0·19	0·09	0·11	0·13	0·04
T	0·61	0·83	0·63	0·53	0·21	0·43	0·28	0·11	0·07	0·15	0·10	0·03
N	0·52	0·63	0·49	0·47	0·18	0·33	0·22	0·07	0·07	0·11	0·08	0·04
W	0·65	0·53	0·73	0·61	0·32	0·27	0·42	0·25	0·12	0·18	0·18	0·04
I	0·51	0·65	0·48	0·41	0·30	0·42	0·35	0·19	0·16	0·24	0·18	0·09

TABLE XXVIII.—Amplitudes of Fourier Waves. (Unit 1γ.)

Element.	Period.	c_1.				c_2.				c_3.				c_4.			
		Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
H	Sunspot maximum	12·83	6·04	14·69	20·57	6·80	4·83	7·66	8·53	2·81	2·57	4·11	2·31	1·27	1·04	1·89	1·03
H	,, minimum	7·21	1·97	8·75	12·68	4·02	2·63	4·82	4·93	2·24	2·00	3·03	2·15	1·10	0·95	1·39	1·01
V	,, maximum	7·84	4·88	7·76	11·18	5·33	2·33	5·77	7·93	1·97	1·15	2·57	2·21	0·65	0·59	0·99	0·38
V	,, minimum	5·44	2·83	5·77	7·97	3·52	1·33	3·87	5·41	1·41	0·67	1·96	1·65	0·54	0·30	0·82	0·49

TABLE XXIX.—Ratios of Amplitudes of Fourier Waves.

Element.	Period.	c_2/c_1.				c_3/c_1.				c_4/c_1.			
		Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
H	Sunspot maximum . . .	0·53	0·80	0·52	0·41	0·22	0·43	0·28	0·11	0·10	0·17	0·13	0·05
H	,, minimum . . .	0·56	1·33	0·55	0·39	0·31	1·01	0·35	0·17	0·15	0·48	0·16	0·08
V	,, maximum . . .	0·54	0·48	0·74	0·71	0·25	0·24	0·33	0·20	0·08	0·12	0·13	0·03
V	,, minimum . . .	0·65	0·47	0·67	0·68	0·26	0·24	0·34	0·21	0·10	0·11	0·14	0·06

Table XXVIII. contrasts the sunspot maximum and minimum values of the amplitude for the year and seasons in both H and V. In H the sunspot maximum value of the amplitude is always the greater. Its excess, however, relatively considered, diminishes as the order of the harmonic increases, and except in c_2 it is least marked in summer.

In V the sunspot maximum value is also always the greater, except in the case of the summer value of c_4; but the pre-eminence of the sunspot maximum value is not specially conspicuous in c_1.

Table XXIX. contrasts the ratios borne to c_1 by c_2, c_3, and c_4 in the seasonal diurnal inequalities in the sunspot maximum and sunspot minimum groups of years. In the case of V the ratios seem little dependent on sunspot frequency, whereas in H with one exception they rise as sunspots diminish, especially in winter. In that season, in fact, in sunspot minimum the amplitude of the 24-hour term is exceeded by that of the 12-hour term and even by that of the 8-hour term.

§ 22. Table XXX. contrasts the phase angles in the diurnal inequalities for the year and seasons in the six elements H, V, T, N, W, and I. An increase in the phase angle as we pass from winter to equinox, and from equinox to summer, is shown by H, N, and T in all four Fourier waves. It is also shown by V in the case of α_4, and by W in the case of α_2. A fall as we pass from winter to equinox, and from equinox to summer, is shown by V in the case of α_1, α_2, and α_3, and by W in the case of α_1. T is remarkable for the smallness of the seasonal variation in the phase angles, especially in the case of α_2.

Table XXXI. contrasts the seasonal and yearly diurnal inequality phase angles in years of sunspot maximum and minimum. In the case of α_2 the sunspot minimum angle is invariably the greater for both H and V. The same is true of α_3, except in the case of H in equinox, when the sunspot minimum angle is slightly the smaller. The same rule is observed by α_4 in H, except in summer; but in V the sunspot maximum value of α_4 is the larger, though its excess is generally small. The sunspot maximum value of α_1 is the larger in summer and winter in H, and in all cases in V.

Table XXXII. shows the difference between the phase angles found in the present paper for ordinary days and those found in a previous paper* for quiet days. It gives the excess of the ordinary day over the quiet day phase angle converted into time at the rate of 1 hour = 15° in α_1, 30° in α_2, 45° in α_3, and 60° in α_4. The plus sign is equivalent to an earlier occurrence of phenomena in ordinary days. The values under the seasons, it should be noticed, are from the seasonal inequalities, and are not arithmetic means from the months included.

The outstanding feature is the preponderance of plus signs in the case of the 24-hour term in V, and the large size of most of the differences from this term.

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* 'Phil. Trans.,' A, vol. 202, p. 335.

TABLE XXX.—Phase Angles Referred to Local Mean Time (11 years' data).

Element.	α_1.				α_2.				α_3.				α_4.			
	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′	° ′	°	°	°	°	°	°	°	°
H	115 23	62 13	107 20	132 9	300 53	276 22	301 44	313 20	169·9	150·4	163·8	203·0	22·6	8·0	19·1	45·5
V	142 43	161 21	140 56	136 40	271 6	282 56	269 32	269 5	100·8	113·7	98·6	97·3	286·0	275·0	288·9	291·1
T	132 33	137 58	127 23	134 48	280 50	279 56	280 16	281 38	125·7	132·1	123·7	123·3	328·3	320·9	326·5	343·2
N	95 48	65 1	91 43	111 38	275 18	257 5	275 41	284 52	138·4	131·9	135·2	159·5	5·3	−15·9	−2·8	42·7
W	219 11	249 16	221 43	204 29	32 53	14 15	31 22	41 14	228·6	228·3	222·4	236·2	51·4	47·0	53·4	53·3
I	285 15	220 52	277 17	310 40	134 58	94 40	136 0	155 57	6·5	−22·8	−1·1	41·7	214·1	197·8	211·7	227·1

TABLE XXXI.—Phase Angles Referred to Local Mean Time.

Element.	Sunspot.	α_1.				α_2.				α_3.				α_4.			
		Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.	Year.	Winter.	Equinox.	Summer.
		° ′	° ′	° ′	° ′	° ′	° ′	° ′	° ′	°	°	°	°	°	°	°	°
H	Maximum . .	114 40	70 55	106 57	132 15	299 15	274 38	301 10	311 7	166·7	144·5	163·2	198·9	20·9	3·2	17·4	45·8
H	Minimum . .	117 31	48 19	108 57	131 53	306 36	286 40	303 15	320 25	173·9	155·1	162·7	208·5	24·4	14·3	19·3	41·3
V	Maximum . .	145 31	162 33	144 50	138 39	269 43	279 56	267 48	268 7	97·1	106·3	94·8	94·9	286·3	278·3	289·5	290·2
V	Minimum . .	137 59	159 18	132 24	134 39	273 42	286 30	271 7	272 26	104·9	124·4	101·2	101·5	283·6	278·2	282·2	289·1

There is obviously a considerable "accidental" element in the results for individual months, especially in the shorter period waves. There is, however, an unmistakable seasonal variation in the phenomena in the 24-hour term in H. In the summer months, the difference, though small, is clearly positive, whereas in winter it is not merely negative but very large, exceeding an hour of time. The fact is the seasonal variation in α_1 in H is much more pronounced in ordinary than in quiet days, the monthly values showing a range of 97° in the first case as compared with 71° in the second.

TABLE XXXII.—Ordinary less Quiet Day Phase Angle in Minutes of Time.

Month and season.	24-hour term.		12-hour term.		8-hour term.		6-hour term.	
	H.	V.	H.	V.	H.	V.	H.	V.
January. . . .	− 68	− 5	+ 8	− 38	− 4	+ 5	− 5	− 8
February . . .	− 60	+ 16	− 1	− 23	− 4	+ 6	+ 6	+ 3
March	− 2	+ 95	+ 1	− 3	− 4	+ 2	− 2	− 4
April	+ 19	+ 76	+ 7	− 3	+ 3	+ 1	+ 13	+ 7
May	+ 8	+ 66	− 14	− 9	+ 5	− 1	+ 4	+ 14
June	+ 3	+ 48	− 9	− 3	+ 8	− 13	+ 24	+ 7
July	+ 12	+ 58	− 2	− 5	+ 15	− 1	+ 18	+ 10
August	+ 5	+ 60	+ 1	− 9	− 1	− 3	− 3	− 9
September. . .	− 31	+ 100	− 25	− 9	− 14	− 2	+ 1	− 14
October	− 25	+ 112	+ 1	− 7	0	− 1	+ 4	+ 8
November. . .	− 69	+ 55	− 7	− 26	− 4	+ 14	0	− 3
December . . .	− 100	+ 67	− 1	− 64	− 5	+ 6	+ 14	− 17
Year.	− 6·2	+ 72·2	− 3·0	− 9·7	− 5·3	+ 0·2	+ 3·8	+ 0·1
Winter	− 82·6	+ 29·8	− 1·8	− 15·8	− 4·5	+ 8·1	+ 2·2	− 4·8
Equinox. . . .	− 9·0	+ 94·9	− 3·4	− 5·5	− 4·7	0·0	+ 3·1	+ 0·1
Summer. . . .	+ 7·5	+ 58·7	− 6·4	− 6·7	+ 5·3	− 4·0	+ 4·8	+ 5·6

The differences in both α_1 and α_2 in V also show a decided seasonal variation. They are algebraically greater in summer than in winter; but in the case of α_1 the equinoctial values are the largest of all.

The variation of α_1 in V in the course of the year is only $42\frac{1}{2}$° in ordinary as compared with $50\frac{1}{2}$° in quiet days. The reduction in the annual range of α_2 in V on ordinary as compared with quiet days is fully larger.

As regards α_3 and α_4 the differences between the ordinary and quiet day phase angles are small, and in the case of V practically evanescent for the mean diurnal inequality of the year. There is an irregularity in the incidence of the plus and minus signs in the case of the α_4 differences which shows the advisability of reserve even as regards the seasonal figures. In the case of α_3 the plus and minus signs show a regular incidence, so that more reliance can be placed on the seasonal values. It will be noticed that the seasonal variations in the two elements are exactly opposite.

Before leaving the subject, attention may be called to the remarkable difference between the phenomena exhibited in the case of a_1 by the different elements. In D the ordinary day phase angle substantially exceeded the quiet day angle throughout the whole year, the excess being greatest in the equinoctial and least in the summer months. The excess in the mean diurnal inequality for the year represented about $29\frac{1}{2}$ minutes* of time. In H the ordinary day phase angle slightly exceeded the quiet day angle in summer, but fell notably short of it in winter, and in the diurnal inequality for the whole year was inferior to an extent representing about 6 minutes of time. In V the ordinary day phase angle substantially exceeded the quiet day angle throughout the year, the excess being greatest in the equinoctial and least in the winter months. In the mean diurnal inequality for the year the excess represented about 72 minutes of time.

WOLF'S *Formula*.

§ 23. If R denote the range of the mean diurnal inequality for the year, and S the sunspot frequency (after WOLF and WOLFER), the formula

$$R = a+b\,S = a\{1+(b/a)S\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with a and b constants, was found by Prof. WOLF to represent closely the variation of the declination range with sunspot frequency. It has been applied by myself to the ranges of the other magnetic elements, and to the individual months or seasons of the year as well as to the whole year. In the case of the quiet day inequalities, the formula applied fairly to all the magnetic elements, being as closely true of H as of D. The value of b/a was, however, not the same for the different elements. Also, when the 12 months were treated separately, b/a fluctuated from month to month, being greatest in winter and least in summer.

The formula has now been applied in the case of both H and V to the diurnal inequalities from ordinary days, for the year, the seasons, and the individual 12 months. The results appear in Table XXXIII.; 1γ is the unit in the case of a and b, and in the mean (numerical) difference between the values calculated by aid of the formula and those actually observed. While a and b are given respectively to 2 and to 4 places of decimals, so as to show the exact values employed in the calculated ranges, the last figure possesses little if any physical significance. Two sets of results are given for the year and the seasons. In the first set the values assigned to a and b are arithmetic means from the individual months included. The corresponding value given for b/a is derived from these mean values of a and b, and is not the arithmetic mean of the values of b/a for the individual months. The second set of figures refers to the diurnal inequalities calculated for the year and seasons.

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* There is a mistake in the description of Table XII. of my previous paper dealing with the declination. The data in it refer not to the seasonal inequalities, but to arithmetic means from the individual months comprised in the season.

Taking, as an example, January in the case of H, the observed ranges in the Januarys of the 11 years were assumed to be given by a formula of type (1), S representing the mean sunspot frequency for each January in succession. The appropriate values of a and b were then determined by least squares, and proved to be $a = 11{\cdot}12\gamma$, $b = 0{\cdot}1358\gamma$. Inserting these values of a and b in the formula, and ascribing to S in succession the frequencies of the 11 Januarys, values were deduced for R. The observed values of R in January fluctuated from $8{\cdot}1\gamma$ in 1899 to $25{\cdot}8\gamma$ in 1892, *i.e.*, they had a range of $17{\cdot}7\gamma$. The sum of the eleven differences between observed and calculated values taken irrespective of sign was $23{\cdot}7\gamma$, the mean difference

TABLE XXXIII.—Constants in WOLF'S Formula $R = a+bS$.

Month and Season.	Horizontal force.					Vertical force.				
	a.	b.	100 b/a.	Mean difference observed ~ calculated.		a.	b.	100 b/a.	Mean difference observed ~ calculated.	
				Absolute value.	As percentage of range.				Absolute value.	As percentage of range.
	γ	γ		γ		γ	γ		γ	
January	11·12	0·1358	1·22	2·2	12·2	5·80	0·0666	1·15	0·8	13·6
February	12·13	0·1495	1·23	1·5	11·4	9·43	0·1060	1·12	1·8	17·1
March	18·31	0·2674	1·46	2·4	12·9	19·26	0·1169	0·61	2·2	16·4
April.	26·83	0·2946	1·10	3·0	12·6	25·45	0·0693	0·27	1·9	15·8
May	30·38	0·2232	0·74	3·8	11·7	27·74	0·1438	0·52	1·6	9·4
June	32·29	0·2561	0·79	3·0	12·1	25·12	0·1213	0·48	1·4	11·2
July	32·43	0·2450	0·75	4·3	14·6	24·56	0·1461	0·59	1·9	12·1
August	32·35	0·1825	0·56	4·2	16·7	23·28	0·0487	0·21	2·2	22·2
September. . . .	26·71	0·1831	0·69	3·1	16·4	16·73	0·1287	0·77	2·0	16·2
October	19·32	0·2635	1·36	2·2	11·2	12·16	0·1271	1·05	1·6	12·6
November. . . .	12·05	0·2195	1·82	2·3	12·3	8·63	0·0942	1·09	1·5	14·7
December	9·67	0·1079	1·12	2·2	15·4	4·99	0·0712	1·43	1·2	12·6
From a.m.s. of *a*'s and *b*'s—										
Year	21·97	0·2107	0·96	2·8	13·3	16·93	0·1033	0·61	1·7	14·5
Winter	11·24	0·1532	1·36	2·0	12·8	7·21	0·0845	1·17	1·3	14·5
Equinox	22·79	0·2522	1·11	2·7	13·3	18·40	0·1105	0·60	1·9	15·2
Summer	31·86	0·2267	0·71	3·8	13·8	25·18	0·1150	0·46	1·8	13·7
From seasonal inequalities—										
Year	18·20	0·2081	1·14	0·5	3·3	16·17	0·1044	0·65	0·8	8·5
Winter	10·78	0·1544	1·43	0·7	6·1	6·79	0·0812	1·20	0·5	6·9
Equinox	20·81	0·2588	1·24	1·2	6·6	17·87	0·1085	0·61	1·4	15·1
Summer	30·95	0·2417	0·78	1·5	6·1	24·58	0·1198	0·49	1·3	9·9

being thus $23\cdot7/11$ or $2\cdot2\gamma$. This expressed as a percentage of the range is $23\cdot7 \times 100/11 \times 17\cdot7$, or $12\cdot2$.

There is obviously a good deal that is "accidental" in the results obtained for individual months, especially in V. The values of b/a, it will be seen, are decidedly larger for H than for V, implying that relatively considered the sunspot influence has more effect on the range of the former element than on that of the latter.

The differences between observed and calculated values naturally tend to increase in size with the extent of the variation of R during the 11 years, and so are largest in summer. The fairest way, however, to compare the accuracy of the formula at different seasons, or for different elements, is to take as criterion the percentage which the mean difference between observed and calculated values is of the difference between the largest and least observed values of R. In H these percentages show no marked variation with the season. There are considerably greater variations in V, but they probably represent in the main the smaller accuracy of observed values in that element, as the largest and smallest values for individual months both fall in summer.

If we exclude the equinoctial value in V, the agreement between observed and calculated values is decidedly closer for the seasons than for individual months, and in the case of H it is still closer, to a marked degree, for the year.

TABLE XXXIV.—Observed less Calculated Ranges in mean Diurnal Inequality for the Year.

Element.	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.
H	$+0\cdot1\gamma$	$+0\cdot6\gamma$	$+0\cdot5\gamma$	$-0\cdot3\gamma$	$+0\cdot4\gamma$	$-0\cdot5\gamma$	$-0\cdot1\gamma$	$0\cdot0\gamma$	$-1\cdot4\gamma$	$+1\cdot3\gamma$	$-0\cdot6\gamma$
V	$-1\cdot7\gamma$	$+1\cdot2\gamma$	$0\cdot0\gamma$	$-1\cdot6\gamma$	$+0\cdot4\gamma$	$0\cdot0\gamma$	$+1\cdot0\gamma$	$+0\cdot8\gamma$	$+1\cdot1\gamma$	$0\cdot0\gamma$	$-1\cdot1\gamma$
I	$+0'\cdot05$	$+0'\cdot05$	$+0'\cdot08$	$+0'\cdot01$	$0'\cdot00$	$-0'\cdot06$	$-0'\cdot07$	$-0'\cdot04$	$-0'\cdot13$	$+0'\cdot13$	$-0'\cdot03$

One's estimate of the suitability of a formula, while mainly determined by the size of the mean difference between observed and calculated values, is partly determined by the mode of grouping of the plus and minus signs. For instance, if the plus signs all occurred together, there would be reason to suspect a sensible secular change in the amplitude of the diurnal inequality, quite apart from sunspot variation. Table XXXIV. accordingly records for each year the actual differences between the observed and calculated values. The calculated values for H and V were derived from the values of a and b assigned in Table XXXIII. to the mean diurnal inequality for the year. The results for I were calculated from

$$a = 0'\cdot8648, \qquad b = 0'\cdot01111,$$

these being the values obtained by the aid of least squares from the observed I range, in the mean diurnal inequalities for the eleven years. The corresponding value of

$100b/a$, viz., 1·28, it may be pointed out, is considerably in excess even of that found for H, and double that found for V. An analogous result was observed in the case of the quiet day ranges.

The plus and minus signs occur pretty promiscuously in Table XXXIV. Also there seems no parallelism between the differences observed in the case of the different elements. In short the differences do not suggest anything but accident. Considering that the observed H ranges varied from 19·6γ to 35·6γ, it seems not a little remarkable that in seven years out of the eleven, the difference between the observed and calculated value did not exceed 0·5γ. The mean difference between observed and calculated values of I was 0′·059, or 6·7 per cent. of the range in I during the eleven years. The agreement is thus closer than in the case of V, though decidedly less good than in the case of H.

§ 24. Wolf's formula was also applied to the observed amplitudes of the 24-, 12-, 8- and 6-hour terms in the mean diurnal inequality for the whole year, in the case of H and V. The results appear in Table XXXV. The agreement between the observed and calculated values is in general good, especially in the case of the 24- and 12-hour terms in H and the 12-hour term in V. It is least good in the case of the 6-hour terms, whose amplitudes even at their largest are very small. The general tendency apparently is for b/a to become smaller, *i.e.*, for the sunspot influence to be less marked, as the order of the harmonic increases, but the 24-hour term in V seems exceptional.

Table XXXV.—Constants in Wolf's Formula $R = a+bS$.

	Horizontal force.					Vertical force.				
	a.	*b.*	$100\,b/a$.	Mean difference observed∼calculated.		*a.*	*b.*	$100\,b/a$.	Mean difference observed∼calculated.	
				Absolute value.	As percentage of range.				Absolute value.	As percentage of range.
	γ	γ		γ		γ	γ		γ	
c_1	6·32	0·0868	1·37	0·27	4·1	5·62	0·0317	0·56	0·40	12·1
c_2	3·49	0·0440	1·26	0·21	6·0	3·42	0·0260	0·76	0·15	7·0
c_3	2·04	0·0103	0·51	0·14	10·5	1·32	0·0090	0·68	0·10	10·0
c_4	1·05	0·0028	0·27	0·04	12·1	0·49	0·0023	0·47	0·05	22·7

The values obtained for *a*, *b*, and b/a for ordinary days in the case of H are very similar to those obtained from the quiet day ranges, but are on the whole slightly larger. In the case of V the differences between ordinary and quiet day results are more marked, and the excess in the b/a from ordinary days over that for quiet days is larger.

Daily Range.

§ 25. The term daily or diurnal range is used in several senses. It may mean the difference R between the algebraically largest and least hourly values in the diurnal inequality, that inequality being derived from selected days or from all days. It may mean, however, the difference R′ between the highest and lowest daily values, irrespective of the time at which they occur, whether an exact hour or not. The mean R′ for a month is simply the arithmetic mean of the values for individual days of the month.

Tables XXXVI. and XXXVII. give R for H and V from ordinary days, for each month of the eleven years. Tables XXXVIII. and XXXIX. give R′ from all days for the same two elements. The R derived from any combination of days must be less than the corresponding R′, unless the maximum and minimum each occur at a fixed time, which is an exact hour. In practice, the times of the maximum and minimum vary from day to day. Speaking generally, the difference between R and R′ for a particular month is larger the more disturbed the month.

If instead of the month one takes the year, the mean R′ is the arithmetic mean of the values for the 12 months, but R is less than the arithmetic mean of the monthly values unless the hours of maximum and minimum in the inequality are the same throughout the year, which is never the case at Kew. Even when one considers the months of the same name from a number of years, there is usually some variation in the hour of maximum or minimum. To bring out these points, Tables XXXVI. and XXXVII. contain the values of R from the inequalities for the whole year and for all the months of the same name combined, as well as the arithmetic means of the values for the individual months.

In Table XXXVI., November is the only month in which the R from the months combined equals the arithmetic mean of the values for the separate months. In the other 11 months the former quantity is the smaller, though the difference is never large. There is a much larger difference between the inequality range for the whole year and the arithmetic mean of the values of R for the twelve months. The former quantity on the average stands to the latter approximately in the ratio 7 : 8.

In Table XXXVII., April is the only month in which R from all the months combined is the same as the arithmetic mean of the values for the individual months, but the differences in the other months are small, just as in the case of H. The differences in Table XXXVII. between the inequality range for the year and the arithmetic mean of the ranges for the twelve months are a good deal smaller than in the case of H. The average excess of the arithmetic means is only about $3\frac{1}{2}$ per cent. This implies, of course, less variability in the hours of maximum and minimum.

Comparing Tables XXXVIII. and XXXIX. with Tables XXXVI. and XXXVII. we see that the excess of R′ over R is usually large. Allowance must, of course, be made for the fact that the more highly disturbed days—242 for H and 348 for V—

TABLE XXXVI.—Horizontal Force. All Ordinary Days. Inequality Ranges. (Unit 1γ.)

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Arithmetic mean.	Inequality for year.
1890	11·9	14·9	20·6	28·7	25·6	33·3	33·5	31·9	30·3	23·3	15·6	13·9	23·6	19·8
1891	13·1	14·0	22·7	35·5	34·5	39·8	44·2	43·0	39·2	38·0	26·2	16·2	30·5	26·2
1892	25·8	25·1	35·2	45·5	45·1	48·4	58·2	55·4	36·3	41·6	24·3	14·3	37·9	33·9
1893	17·8	22·8	36·5	51·0	46·5	57·6	57·2	51·9	43·8	40·7	30·2	23·0	39·9	35·6
1894	21·7	24·7	31·6	49·6	58·0	57·9	50·8	52·2	41·2	37·8	23·4	18·7	39·0	34·8
1895	18·1	23·0	38·0	50·7	45·2	56·5	52·5	37·3	33·9	33·1	24·2	16·7	35·8	31·0
1896	19·1	21·5	29·8	44·5	40·7	38·9	40·0	42·3	40·3	25·6	15·0	9·8	30·6	26·8
1897	17·9	17·6	25·9	42·7	40·8	37·7	36·7	33·1	28·8	24·2	12·4	12·4	27·5	23·6
1898	14·9	12·2	22·2	26·9	36·0	41·9	39·0	34·7	31·3	23·7	17·8	9·9	25·9	22·4
1899	8·1	14·6	19·8	28·1	37·7	38·1	36·8	34·8	34·9	22·2	16·7	10·7	25·2	22·0
1900	13·5	13·3	23·5	26·8	30·1	33·1	28·7	30·3	24·7	23·4	11·3	8·5	22·3	19·6
Arithmetic mean . .	16·5	18·5	27·8	39·1	40·0	43·9	43·4	40·6	35·0	30·3	19·7	14·0	30·7	26·9
11-year inequality .	16·0	18·1	26·7	38·3	39·9	43·8	43·1	40·2	34·5	29·9	19·7	13·6	—	—

Table XXXVII.—Vertical Force. All Ordinary Days. Inequality Ranges. (Unit 1γ.)

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Arithmetic mean.	Inequality for year.
1890	5·7	11·3	19·0	24·2	25·5	24·2	25·3	18·8	17·0	9·2	5·6	3·1	15·7	15·2
1891	6·2	8·3	23·7	28·6	32·8	30·2	34·0	28·9	23·3	21·2	13·7	10·0	21·7	21·1
1892	11·7	16·6	30·8	27·8	40·3	33·1	36·2	28·2	23·8	22·0	12·1	10·7	24·4	23·8
1893	10·9	14·3	22·0	30·6	37·1	36·3	39·2	27·0	28·3	20·9	15·6	12·9	24·6	23·4
1894	10·3	18·2	24·6	33·2	42·2	36·1	36·8	28·8	28·5	21·2	15·8	9·0	25·4	24·7
1895	10·2	18·9	26·6	30·5	39·0	36·2	36·3	25·8	18·7	20·0	15·2	8·4	23·8	22·8
1896	10·2	17·5	27·8	29·3	31·9	31·0	30·6	27·6	24·7	17·2	10·6	7·7	22·2	21·5
1897	7·5	14·4	23·4	29·9	33·5	28·0	25·8	26·0	22·3	16·0	10·5	5·2	20·2	19·7
1898	6·2	15·3	21·9	27·8	33·6	30·8	28·7	26·4	24·3	16·1	11·8	6·0	20·7	20·1
1899	6·8	9·6	20·6	28·5	29·5	25·1	26·0	20·6	20·6	12·5	10·7	7·9	18·2	17·4
1900	7·2	9·1	17·1	21·2	27·9	25·9	23·3	22·3	16·4	15·8	9·6	5·5	16·8	16·1
Arithmetic mean .	8·4	14·0	23·4	28·3	33·9	30·6	31·1	25·5	22·5	17·5	11·9	7·9	21·2	20·5
11-year inequality .	7·9	13·8	23·0	28·3	33·6	30·4	30·9	25·3	22·1	17·0	11·5	7·1	—	—

contributed to R′ but not to R. If they had been excluded in both cases, R′ would have been appreciably reduced, more especially in the equinoctial months and in the years 1892, 1894, and 1896; while, if they had been included in both cases, R would probably have been slightly increased.

TABLE XXXVIII.—Horizontal Force. All Days. Absolute Ranges. (Unit 1γ.)

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Mean.
1890	35·1	43·1	39·6	46·3	40·3	47·4	50·5	52·6	55·8	54·1	41·8	31·4	44·8
1891	34·9	47·4	66·8	74·6	75·9	60·0	61·4	69·3	74·3	71·4	50·7	43·0	60·8
1892	56·2	113·0	114·1	83·9	91·2	83·1	117·3	96·1	70·6	74·6	54·9	53·4	84·0
1893	55·4	59·1	67·6	77·5	65·3	85·7	83·1	88·5	79·8	71·5	60·4	43·1	69·7
1894	61·6	98·5	78·3	78·8	82·8	95·0	106·4	95·1	88·6	71·9	74·2	46·2	81·4
1895	47·4	66·0	75·6	81·3	76·2	82·3	80·5	58·0	62·7	73·3	64·4	46·5	67·9
1896	63·5	68·2	68·5	74·4	78·7	60·5	68·0	75·7	76·9	58·1	43·1	38·9	64·5
1897	40·0	41·8	51·8	77·6	68·9	55·6	53·9	51·2	48·3	50·7	37·8	44·1	51·8
1898	39·4	49·0	73·1	51·7	64·6	62·3	60·3	61·7	77·0	54·8	40·0	37·8	56·0
1899	39·3	42·1	50·4	55·9	64·7	60·5	55·0	57·1	59·9	41·7	33·6	35·0	49·6
1900	39·1	33·4	47·8	41·4	48·6	43·5	40·2	42·6	36·1	34·7	22·7	18·1	37·3
Mean .	46·5	60·1	66·7	67·6	68·8	66·9	70·6	68·0	66·4	59·7	47·6	39·8	60·7

TABLE XXXIX.—Vertical Force. All Days. Absolute Ranges. (Unit 1γ.)

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Mean.
1890	16·6	20·6	26·5	27·2	28·4	26·8	25·8	23·0	21·9	22·0	15·5	3·6	21·5
1891	15·5	23·9	35·9	42·8	53·7	31·6	35·8	33·5	47·3	32·2	25·5	24·8	33·5
1892	25·0	65·8	74·9	49·0	68·4	52·2	68·0	48·3	33·0	39·9	28·3	32·8	48·8
1893	27·0	33·1	34·1	35·3	38·6	44·0	44·7	46·9	39·9	34·6	37·4	24·4	36·7
1894	28·8	68·6	52·8	45·7	44·9	45·9	65·8	48·7	58·0	29·1	45·8	21·8	46·3
1895	23·8	38·8	38·9	40·8	44·0	43·3	38·6	30·8	30·7	40·6	32·6	24·0	35·6
1896	28·8	34·7	44·8	37·8	51·7	32·4	36·2	37·2	32·7	30·0	22·6	22·3	34·3
1897	23·5	21·2	28·9	44·1	37·9	29·4	28·0	27·8	23·8	20·7	16·6	19·3	26·8
1898	17·2	26·1	53·3	30·8	36·4	30·8	29·3	33·0	44·1	27·6	22·9	18·0	30·8
1899	21·1	25·5	29·2	31·7	33·0	33·2	29·2	24·6	24·3	17·7	14·9	17·4	25·1
1900	19·0	16·8	27·0	23·4	34·8	26·8	25·8	26·0	19·3	19·7	13·9	12·8	22·1
Mean	22·4	34·1	40·6	37·1	42·9	36·0	38·8	34·5	34·1	28·6	25·1	20·1	32·9

§ 26. Table XL. gives the ratio borne by the mean R′ to the corresponding arithmetic mean of the values of R for the 12 months and for the 11 years separately. The disturbed days omitted from the V inequalities were the more numerous, so that any reduction in R consequent on this exclusion would naturally be greater in V than in H. The excess of R′ is, however, invariably much larger for H than for V, confirmatory of what has been already said as to the former being in general much the more disturbed element. Relatively considered, the excess of R′ over R has a conspicuous maximum near mid-winter, and a minimum near mid-summer. The pre-eminence of the values of R′/R in winter over those in equinoctial months is hardly what one would have expected from consideration of disturbances alone. We see that the size of the regular diurnal inequality is apt to give in winter a very inadequate idea of the average diurnal variation in the field.

TABLE XL.—Values of (Absolute Range from All Days)/(Inequality Range from Ordinary Days).

Element.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Mean.
H	2·81	3·25	2·40	1·73	1·72	1·52	1·63	1·67	1·90	1·97	2·41	2·84	2·13
V	2·65	2·44	1·73	1·31	1·26	1·18	1·25	1·35	1·51	1·64	2·10	2·56	1·75

	1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.	Mean.
H	1·90	1·99	2·22	1·74	2·09	1·90	2·11	1·88	2·16	1·97	1·67	1·97
V	1·37	1·54	2·00	1·49	1·82	1·49	1·55	1·32	1·49	1·38	1·32	1·52

If we compare the values of R′/R in different years, we see that while on the whole it was least in the years of fewest sunspots, it was considerably below average in 1893, the year of sunspot maximum. In the case of H, in fact, it was lower for 1893 than for any other year except 1900. This means that in 1893 R was specially large, and not that R′ was small. As Table XXXVIII. shows, the mean value of R′ for 1893 was 15 per cent. above the average of the 11 years, and was exceeded only in 1892 and 1894. In the case of V the value of R′/R for 1893, though less remarkable, was below the mean. In both H and V the values of R′ for 1892 and 1894 were much in excess of that for 1893. For 1892 this excess was 21 per cent. for H, and 33 per cent. for V.

Table XLI. shows the order in which the years stand when placed in descending order of range. Data for D are included to make the survey more complete. The resulting order is also shown when the figures from D, H and V are added, and finally the order when the sunspot frequency is the criterion. R and R′ are treated separately.

When the size of R′ is the criterion, the order is the same for all the magnetic elements, except that 1890 comes last in V, while 1900 comes last in D and H.

There is less agreement between the results from the three elements in the case of R, but the differences between the pairs of years 1890 and 1900, 1892 and 1894, and last 1897 and 1898, are so small that little significance attaches to the precise order in which the members of the pair present themselves. In the final returns from the three elements combined, the only difference between the R and R′ lists is that there is an interchange of place between 1892 and 1893, and between 1897 and 1898.

Table XLI.—Position of Years when Arranged in Descending Order of R, R′, and S.

		1890.	1891.	1892.	1893.	1894.	1895.	1896.	1897.	1898.	1899.	1900.
R	D	9	6	2	1	3	4	5	7	8	10	11
	H	10	6	3	1	2	4	5	7	8	9	11
	V	11	6	3	2	1	4	5	8	7	9	10
	Mean . .	10	6	3	1	2	4	5	7	8	9	11
R′	D	10	6	1	3	2	4	5	8	7	9	11
	H	10	6	1	3	2	4	5	8	7	9	11
	V	11	6	1	3	2	4	5	8	7	9	10
	Mean . .	10	6	1	3	2	4	5	8	7	9	11
Sunspots		11	6	3	1	2	4	5	8	7	9	10

Table XLII. deals with the twelve months in the same way that Table XLI. dealt with the eleven years. In Table XLII. the points of agreement between the different elements in the same list, or between the same element in the two lists, are somewhat inconspicuous outside the mid-winter months. Successive months sometimes occupy very different positions, without there being a very large difference between their values of the ranges. A longer period of years would be required to eliminate satisfactorily what is accidental. Whether one takes R or R′, it is clear that December, January, and November fill the last three places.

When the three elements are combined, May, July, and August are bracketed second in the case of R. In the case of R′ there is a bracket between April and July, and again between June and September.

The difference between the positions occupied by June in the R and R′ lists is remarkable. In the R list it comes first, slightly in advance of the other three mid-summer months, whereas in the R′ list no element places it higher than fifth.

Another striking phenomenon is the difference between the positions assigned to March and July in the R′ list according as the element considered is D or H. In the case of H, it is true, the mean values of R′ for the six months March to September differ comparatively little. Still the fact that (July Range/March Range) = 0·88 for D, but = 1·06 for H, appears a little remarkable.

TABLE XLII.—Position of Months when Arranged in Descending Order of R and R′.

		January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
R	D	11	9	7	2	4	3	5	1	6	8	10	12
	H	11	10	8	5	4	1	2	3	6	7	9	12
	V	11	9	6	4	1	3	2	5	7	8	10	12
	Mean .	11	9	7	5	(2)	1	(2)	(2)	6	8	10	12
R′	D	11	8	1	2	3	9	6	5	4	7	10	12
	H	11	8	6	4	2	5	1	3	7	9	10	12
	V	11	7	2	4	1	5	3	6	8	9	10	12
	Mean .	11	8	2	(3)	1	(6)	(3)	5	(6)	9	10	12

§ 27. In the case of the mean diurnal inequality for the year there is, as we have seen, a close connection between the range and the corresponding sunspot frequency S. This does not necessarily imply any close connection between sunspot frequency on any given day and the amplitude of the regular or irregular magnetic changes on the same day. It seems increasingly difficult to think of any cause for the magnetic diurnal inequality other than electrical currents in the upper atmosphere. In temperate latitudes, whether at sunspot maximum or minimum, regular magnetic changes are most rapid during the day, but the difference between day and night seems reduced at sunspot maximum. Whether by day or by night, the regular changes are larger in sunspot maximum than in sunspot minimum. The most natural inference is that direct sunlight, whether there are or are not sunspots, increases the conductivity of the upper atmosphere, and that the effect persists to some extent during the night. At sunspot maximum the upper atmosphere is more conducting than at sunspot minimum at the same hour. The state of the upper atmosphere as regards conductivity may be due to contributions from some, perhaps many, previous days. The solar influences may be of different kinds, taking different times to travel from the sun and decaying at different rates. Sunspots again may be evidence of some effect on the sun which is shared by the solar system, but which takes some time to travel the distance separating the earth from the sun. The diurnal inequality can be derived only from a combination of days. Thus it does not enable us to compare magnetic conditions and sunspot frequency on individual days. There is even a difficulty in comparing the run of magnetic conditions and sunspots during successive months, owing to the annual variation in the daily range. This difficulty can, however, be fairly surmounted if we express the range for each month as a percentage of the mean range from all months of the same name in the 11-year period. The percentage values thus obtained for R and R′ in H appear in Table XLIII. along with the corresponding WOLFER's sunspot frequency, the latter in heavy type.

The general tendency for the percentage figures in Table XLIII. to be large in years of many, and small in years of few sunspots, is of course obvious. But when we compare successive months, we see that with rise of S we may have rise or fall of R, and that R and R′ not infrequently change in opposite directions. There being 132 months, there are 131 passages from one month to the next. If we allow 1/2 in cases where the value is the same in two consecutive months, we find that R and R′ changed in the same direction in 84 cases, S and R changed in the same direction in $65\frac{1}{2}$ cases, while S and R′ changed in the same direction in $72\frac{1}{2}$ cases. A large monthly value for R′ may be due to only two or three highly disturbed days, excluded from the ordinary days, still the number of cases in which R and R′ changed in opposite direction is larger than would have been expected. The figures quoted above, by themselves, afford no evidence of a connection between S and R in individual months, and only slight evidence of a connection between S and R′. This differs from what was observed in the case of D. There R and S increased or diminished together in 75 cases out of 131, while R′ and S increased or diminished together only in 68 cases.

In many instances the values of S for consecutive months differ so little that accident might play a considerable part. If we confine ourselves to the 52 cases in which S changed by at least 10 units, there was agreement in the direction of change

in 30 cases as between R and S,
,, 28 ,, ,, R′ ,, S,
,, 34 ,, ,, R ,, R′.

This is decidedly more favourable to a connection between R and S in individual months.

In a second investigation the months of each year were arranged in two groups of 6, consisting respectively of the months of largest and least sunspot frequency. The

TABLE XLIII.—Comparison of Sunspot Frequencies and H Range Percentages.

Year.		January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
1890	S	5·3	0·6	5·1	1·6	4·8	1·3	11·6	8·5	17·2	11·2	9·6	7·8
	R	72	80	74	73	64	76	77	79	87	77	79	99
	R'	75	72	59	68	59	71	72	77	84	91	88	79
1891	S	13·5	22·2	10·4	20·5	41·1	48·3	58·8	33·2	53·8	51·5	41·9	32·2
	R	79	76	82	91	86	91	102	106	112	125	133	116
	R'	75	79	100	110	110	90	87	102	112	120	107	108
1892	S	69·1	75·6	49·9	69·6	79·6	76·3	76·8	101·4	62·8	70·5	65·4	78·6
	R	157	136	127	116	113	110	134	136	104	137	123	102
	R'	121	188	171	124	133	124	166	141	106	125	115	134
1893	S	75·0	73·0	65·7	88·1	84·7	88·2	88·8	129·2	77·9	79·7	75·1	93·8
	R	108	123	131	130	116	131	132	128	125	134	153	164
	R'	119	98	101	115	95	128	118	130	120	120	127	108
1894	S	83·2	84·6	52·3	81·6	101·2	98·9	106·0	70·3	65·9	75·5	56·6	60·0
	R	131	134	114	127	145	132	117	129	118	125	119	134
	R'	132	164	117	117	120	142	151	140	133	120	156	116
1895	S	63·3	67·2	61·0	76·9	67·5	71·5	47·8	68·9	57·7	67·9	47·2	70·7
	R	110	124	137	130	113	129	121	92	97	109	123	119
	R'	102	110	113	120	111	123	114	85	94	123	135	117
1896	S	29·0	57·4	52·0	43·8	27·7	49·0	45·0	27·2	61·3	28·4	38·0	42·6
	R	116	116	107	114	102	89	92	104	115	84	76	70
	R'	137	114	103	110	114	90	96	111	116	97	90	98
1897	S	40·6	29·4	29·1	31·0	20·0	11·3	27·6	21·8	48·1	14·3	8·4	33·3
	R	108	95	93	109	102	86	85	82	82	80	63	89
	R'	86	70	78	115	100	83	76	75	73	85	79	111
1898	S	30·2	36·4	38·3	14·5	25·8	22·3	9·0	31·4	34·8	34·4	30·9	12·6
	R	90	66	80	69	90	95	90	85	89	78	90	71
	R'	85	81	110	77	94	93	85	91	116	92	84	95
1899	S	19·5	9·2	18·1	14·2	7·7	20·5	13·5	2·9	8·4	13·0	7·8	10·5
	R	49	79	71	72	94	87	85	86	100	73	85	76
	R'	85	70	76	83	94	90	78	84	90	70	71	88
1900	S	9·4	13·6	8·6	16·0	15·2	12·1	8·3	4·3	8·3	12·9	4·5	0·3
	R	82	72	85	69	75	75	66	75	71	77	57	61
	R'	84	56	72	61	71	65	57	63	54	58	48	46

mean values obtained for S and for the percentage values of R and R′ in H for the two groups appear in Table XLIV.

TABLE XLIV.—Percentage H Ranges from Groups of Months of Larger and Smaller Sunspot Frequency.

Year.	Group of months of largest sunspot frequency.			Group of months of least sunspot frequency.		
	S.	R per cent.	R′ per cent.	S.	R per cent.	R′ per cent.
1890	11·0	83	82	3·1	73	67
1891	49·2	108	104	22·0	92	96
1892	81·4	122	148	64·6	127	127
1893	95·5	133	116	74·4	129	114
1894	92·6	131	138	63·4	123	130
1895	70·6	115	113	57·4	119	111
1896	51·4	106	105	32·2	92	108
1897	35·3	96	89	17·2	83	83
1898	34·4	81	96	19·1	84	88
1899	16·5	73	80	7·7	87	83
1900	13·2	75	66	5·7	69	57
Mean . . .	50·1	102·1	103·4	33·3	98·0	96·7

The higher R′ percentage appears in the group of higher values of S in 9 years out of the 11. In the two exceptional years, 1896 and 1899, the deficiency in the value of R′ in the first group is only 3, and so possesses little significance. On the average of the eleven years, the excess of the percentage values of R′ in the first group amounts to 6·7. If we regard this as a percentage on $60{\cdot}7\gamma$, the mean value of R in H for the eleven years, we get $4{\cdot}0_7\gamma$ as corresponding to a difference of 16·8 in S. On a formula of the type $R' = a+b\,S$, this would give

$$100\,b/a = 0{\cdot}47.$$

In the case of R the higher percentage value is associated with the higher value of S in 7 years. In one of the 4 exceptional years, 1899, the deficiency in R is substantial, but this possesses less significance than would otherwise be the case from the fact that the difference between the values of S for the two groups in that year is little over half the average. The excess in the percentage value of R in the group of higher values of S, on the average of the 11 years, is 4·1. If we regard this as a percentage on $30{\cdot}7\gamma$, the mean value of R in H from the 132 months, we get $1{\cdot}26\gamma$ as corresponding to a difference of 16·8 in S. On a formula of the type $R = a+b\,S$, this would give

$$100\,b/a = 0{\cdot}27.$$

Taking the arithmetic mean of the monthly values of R in H for each year of the eleven, and applying the $R = a + b\,S$ formula, I found by least squares

$$a = 21{\cdot}47\gamma, \quad b = 0{\cdot}2224\gamma, \quad 100\,b/a = 1{\cdot}036.$$

The division of the year into equal groups of 6 months only partly attains the object in view, viz., the elimination of any cause whose effect lasts for several months, because there is some tendency for the months of higher S in a year to occur together. In 1890, for instance, the 6 months of largest S came from the second half of the year, while in 1894 and 1900 the first half of the year contributed 5 out of the 6 months in the first group. Taking this into account, and the smallness of the value of b/a deduced in the case of R from Table XLIV., the natural inference would seem to be that the value of R from ordinary days in a particular month depends less on the value of S in that month than on the values of S in the other months of the year.

This may mean nothing more than that the value of S on a particular day is a very rough measure of the solar activity to which enhanced diurnal inequalities are due, while the mean value of S from all days of the year affords a very exact measure.

The fact that the value of b/a derived from Table XLIV. in the case of R′ is so much larger than that derived in the case of R, suggests that the solar influence is more direct or immediate in the case of irregular than in the case of regular magnetic changes.

Table XLV. shows the result of grouping the 132 months according to the monthly mean value of S. Notwithstanding the considerable number of months included in the groups, the results of the first grouping in which the step in S is only 10 are somewhat irregular. R and R′ show a decided tendency throughout to increase with

TABLE XLV.—Percentage Ranges from Months Grouped according to Sunspot Frequency.

Range of values of S.	Months in group.	Mean values:			Range of values of S.	Months in group.	Mean values.		
		S.	R per cent.	R′ per cent.			S.	R per cent.	R′ per cent.
0 to 10	23	6·2	77·8	71·5	0 to 20	43	9·6	76·6	74·4
10 „ 20	20	13·8	75·1	77·7	20 „ 40	26	29·1	91·4	96·5
20 „ 30	14	25·1	93·0	94·6	40 „ 60	20	49·3	106·4	109·2
30 „ 40	12	33·7	89·5	98·7	60 „ 80	30	70·6	123·0	121·7
40 „ 50	12	45·4	103·0	106·7	>80	13	94·6	132·5	127·8
50 „ 60	8	55·0	111·5	112·9					
60 „ 70	14	65·4	120·2	112·6					
70 „ 80	16	75·2	125·4	129·6					
80 „ 90	7	85·6	128·7	124·1					
>90	6	105·1	137·0	132·0					

S, but in the group or groups with S above 80 the rate of increase seems reduced. The exceptionally high monthly values of S occurred sporadically. For instance, the extreme value, 129·2 in August 1893, was preceded by 88·8 in July and followed by 77·9 in September. Thus we should not expect a correspondingly high value of R unless the influence of previous months is negligible.

In considering the significance of Table XLV. allowance should be made for the fact that some of the groups come entirely from years of sunspot maximum. No value of S as high as 60 occurred in the sunspot minimum or intermediate years. Again, sunspot minimum years gave no value of S larger than 20·5, and so their contributions were practically confined to the groups 0 to 10 and 10 to 20. Intermediate years contributed only two months to the group 0 to 10, and six to the group 10 to 20.

§ 28. We have hitherto considered only mean monthly values of R′, but the way in which these values are made up seems also of interest. To make the results more complete, D has been included in the investigation. Some data for D were got out in a previous paper,* but they are considerably extended here. As a preliminary it is well to know something about the extreme values of R′. To this end Tables XLVI. and XLVII. give the smallest recorded values of R′ in D and H for each month.

TABLE XLVI.—Declination. Absolute Daily Ranges. Smallest Values.

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Year.
	′	′	′	′	′	′	′	′	′	′	′	′	′
1890	4·2	5·6	5·1	8·2	6·2	6·9	8·0	8·2	5·0	5·7	5·0	3·8	3·8
1891	3·1	4·1	4·3	8·1	8·5	7·9	8·6	9·2	9·8	7·9	7·1	4·7	3·1
1892	5·7	8·3	11·4	10·9	10·3	9·2	11·4	10·1	9·2	8·5	3·7	5·7	3·7
1893	5·0	5·0	8·0	12·5	11·9	12·3	11·6	11·5	10·1	9·3	5·9	4·1	4·1
1894	6·8	7·9	8·3	9·6	10·6	10·5	6·8	9·7	10·3	9·0	4·7	4·6	4·6
1895	3·9	6·8	8·3	11·9	10·0	13·0	10·8	8·0	8·5	8·6	5·2	3·8	3·8
1896	6·0	7·3	8·0	10·9	9·0	6·7	7·9	9·8	8·2	6·6	3·4	2·7	2·7
1897	3·2	4·3	8·9	8·3	7·4	7·8	8·0	9·1	6·1	5·8	4·3	2·2	2·2
1898	3·1	3·5	6·0	8·0	7·1	7·7	7·2	8·0	7·5	6·5	4·3	3·3	3·1
1899	3·0	3·8	6·3	7·9	7·1	8·4	6·4	8·2	7·7	4·2	3·0	2·4	2·4
1900	3·2	3·1	5·3	7·2	5·7	7·8	8·0	6·5	5·6	5·1	2·2	2·5	2·2
Whole period.	3·0	3·1	4·3	7·2	5·7	6·7	6·4	6·5	5·0	4·2	2·2	2·2	2·2

Corresponding data are not given for V owing to their greater uncertainty. V ranges are on the average less than D or H ranges, and when very small they are

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* 'Phil. Trans.,' A, vol. 208, p. 205.

exposed to undue uncertainty owing to the large temperature coefficient of the magnet and the absence of a temperature correction. The uncorrected temperature effect on R′ is of course not always in one direction, but amongst the least ranges of the month the chances are that some will be reduced by the temperature effect. Thus the natural consequence of the absence of a temperature correction will be to give too low a value for the monthly minimum range. The H ranges are not wholly free from this uncertainty, but the temperature coefficient of the H magnet is only about a seventh of that of the V magnet, while the average range in H is fully 80 per cent. in excess of that in V, thus the uncertainty is of quite a different order.

TABLE XLVII.—Horizontal Force. Absolute Daily Ranges.
Smallest Values (Unit 1γ).

Year.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Year.
1890	16	18	17	31	25	26	31	24	23	25	16	13	13
1891	12	17	18	38	28	35	39	41	40	29	29	13	12
1892	26	36	37	30	41	44	46	45	36	38	19	17	17
1893	20	20	31	52	40	45	42	50	38	36	30	19	19
1894	21	30	25	36	46	60	50	49	31	36	22	19	19
1895	16	29	34	50	45	52	44	27	33	30	21	16	16
1896	24	29	23	43	35	35	29	33	48	23	15	12	12
1897	13	15	24	34	36	33	31	28	27	21	18	12	12
1898	10	13	29	16	23	33	28	25	33	23	18	11	10
1899	11	16	22	30	31	27	22	32	37	16	13	9	9
1900	12	12	21	25	26	29	23	22	22	14	11	7	7
Whole period	10	12	17	16	23	26	22	22	22	14	11	7	7

The D range is entirely free from this source of uncertainty, so far as is known; it has the further advantage that no error can arise from an unrecognised variation in the scale value. There is, however, one slight drawback attending it, viz., that the force required to alter D by 1′ alters if H alters. Strictly speaking, the force equivalent to a change of 1′ in D is different at different times of a highly disturbed day.

The slight increase in accuracy that would result from allowing for changes in H in the course of a single day would be no adequate return for the labour involved. Apart from any disturbance effect, the force equivalent to a change of 1′ in D is influenced by secular change in H. The mean value of H in 1900 exceeded that in

1890 by 259γ, or about 1·4 per cent. If we go to 3 figures, the force required to alter D by 1′ was

5·29γ in 1890 and 1891
5·30γ ,, 1892
5·31γ ,, 1893 and 1894
5·32γ ,, 1895
5·33γ ,, 1896
5·34γ ,, 1897 and 1898
5·35γ ,, 1899
5·36γ ,, 1900.

This variation, though quite appreciable when we are dealing with large ranges, is hardly worth considering in the case of the minimum ranges in Table XLVI.

Examining that table we see that the winter months, especially December, are conspicuous for small ranges. The fact that the mean values of R′ for winter months fall conspicuously short of those for other seasons is due, not so much to the absence of large values of R′, as to the presence of a considerable number of very small values. In summer, really small ranges are scarce. In fact, in the half year from April to September no single day of the 11 years had a range under 5′. In 1893 no April day had a range under 12′·5, though the mean value for the month was only 17′·1, and in June the lowest range was 12′·3 though the mean for the month was only 16′·4. The uniformity of the range in June 1893 was very remarkable. In 21 of the 30 days the range lay between 14′·0 and 18′·5 and the highest value of the month was only 21′·6. The absolutely smallest range of the 11 years was 2′·2, or 12γ in force.

Turning to Table XLVII., we see that the lowest range recorded was 7γ. The winter months, as with D, supply all the outstandingly small ranges, December being especially conspicuous.

During the eleven years the sensitiveness of the Kew H magnetograph was always near 1 mm. = 5γ. Thus a range of 7γ implies a variation of only 1·4 mm. in the length of the ordinate throughout a portion of curve whose length of abscissa is 360 mm. This means a slope so gentle everywhere that the recognition of the positions of the maximum and minimum is no easy matter. Again, a change of 1° F. in temperature would alter the ordinate fully 0·3 mm. Thus not improbably 7γ may have been somewhat an under-estimate of the true minimum range.

At the other end of the scale the largest observed ranges were

in D, 1° 25′·6 ($\equiv$457γ) on March 15, 1898 ;
in H, 720γ on February 13, 1892 ;
in V, 639γ on July 20, 1894.

It is possible that the D range on March 15, 1898, may have been exceeded on

February 14, 1892, as the trace then went beyond the limit of registration, and the range measured to the edge of the sheet was 1° 19′. If we accept the value on March 15, 1898, as the true maximum, we find maximum range/minimum range = 102·9 in H, as compared with 39·4 in D.

§ 29. Tables XLVIII. to LIII. deal with the frequency of occurrence of ranges of different size for D, H, and V. There are two tables for each element, the one showing the distribution for each of the 11 years, the other the distribution for each of the 12 months. To make the D results comparable with those for the force elements, the same force limits are employed for the several classes. It was not necessary to convert individual D ranges into their equivalents in force, but only to find what were the angles corresponding to the several force limits, employing the relation between 1′ and 1γ appropriate to the particular year.

TABLE XLVIII.—Declination Ranges (Unit 1γ). Number of Occurrences.

Year.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
1890	0	4	55	96	96	68	30	11	4	1	0	0	0	0
1891	0	13	27	35	78	75	80	37	8	5	4	2	1	0
1892	0	1	9	28	49	70	115	39	18	12	9	8	8	0
1893	0	3	13	26	33	61	156	47	15	8	2	0	1	0
1894	0	2	10	36	41	92	107	36	15	4	7	3	12	0
1895	0	6	18	27	49	70	112	41	19	16	7	0	0	0
1896	0	8	26	36	65	82	75	36	18	11	3	5	1	0
1897	1	15	37	57	93	74	45	31	6	2	1	1	2	0
1898	0	17	39	52	102	66	52	22	8	2	2	0	3	0
1899	0	26	38	70	93	64	50	12	3	5	2	2	0	0
1900	1	49	49	96	102	45	14	3	3	3	0	0	0	0

TABLE XLIX.—Declination Ranges (Unit 1γ). Number of Occurrences in Eleven Years.

Month.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
January. . .	0	38	67	74	51	30	37	23	10	6	1	3	1	0
February . .	0	21	43	52	44	42	54	26	9	7	4	3	5	0
March. . . .	0	1	11	39	71	68	67	36	24	14	3	1	6	0
April	0	0	0	25	74	85	90	32	12	5	5	1	1	0
May.	0	0	6	40	61	82	97	29	14	4	1	5	2	0
June	0	0	2	35	88	89	84	23	2	4	0	3	0	0
July.	0	0	2	32	96	97	80	19	3	4	2	3	3	0
August . . .	0	0	1	19	86	93	110	24	4	2	0	0	2	0
September .	0	0	8	36	81	70	87	23	11	3	7	1	3	0
October. . .	0	1	21	69	66	43	68	45	13	8	7	0	0	0
November .	1	30	64	70	50	40	32	16	8	10	6	1	2	0
December. .	1	53	96	68	33	28	30	19	7	2	1	0	3	0

Table L.—Horizontal Force Ranges (Unit 1γ). Number of Occurrences.

Year.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
1890	0	40	99	111	66	28	14	5	2	0	0	0	0	0
1891	1	23	49	68	82	52	59	14	11	3	1	1	1	0
1892	0	4	33	66	61	60	68	29	16	4	3	9	10	3
1893	0	10	32	50	81	68	78	25	13	5	0	3	0	0
1894	0	8	44	38	59	71	79	32	12	5	4	2	9	2
1895	0	9	38	57	77	66	68	30	10	8	2	0	0	0
1896	2	26	42	68	72	51	60	26	11	3	3	0	2	0
1897	1	34	69	99	78	39	27	9	6	2	1	0	0	0
1898	3	46	58	80	67	46	41	17	2	1	1	1	0	2
1899	4	45	83	79	69	37	33	9	5	1	0	0	0	0
1900	15	73	117	106	32	11	7	1	1	1	0	1	0	0

Table LI.—Horizontal Force Ranges (Unit 1γ). Number of Occurrences in Eleven Years.

Month.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
January . .	5	73	97	58	32	32	22	12	7	0	1	1	1	0
February . .	1	45	73	48	49	30	30	14	11	1	2	1	3	2
March . . .	0	12	71	71	68	32	38	21	15	2	2	3	5	1
April	0	2	29	73	64	66	62	19	4	6	2	2	1	0
May	0	1	36	64	80	64	60	18	6	4	2	2	4	0
June	0	0	29	75	78	58	55	14	13	4	1	2	1	0
July	0	2	38	69	78	49	61	24	9	3	1	3	3	1
August . . .	0	5	23	77	94	56	53	21	4	3	1	2	0	2
September .	0	5	32	76	79	52	55	16	7	3	1	0	3	1
October . . .	0	15	61	79	46	48	66	21	1	2	2	0	0	0
November .	3	67	78	78	47	18	17	9	9	3	0	0	1	0
December .	17	91	97	54	29	24	15	8	3	2	0	1	0	0

Table LII.—Vertical Force Ranges (Unit 1γ). Number of Occurrences.

Month.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
1890	71	164	111	13	5	1	0	0	0	0	0	0	0	0
1891	26	110	143	39	22	7	7	5	4	1	0	0	1	0
1892	13	96	126	58	17	12	15	8	3	3	2	3	9	1
1893	6	106	126	75	23	9	13	3	1	1	1	1	0	0
1894	15	96	134	52	26	12	10	3	2	1	2	3	7	2
1895	13	101	136	53	31	12	13	5	1	0	0	0	0	0
1896	18	127	127	40	21	10	13	7	1	0	1	1	0	0
1897	51	144	119	26	13	2	7	0	2	1	0	0	0	0
1898	37	132	133	40	13	3	3	1	0	0	0	0	2	1
1899	45	170	108	27	5	3	6	0	1	0	0	0	0	0
1900	61	199	94	6	3	0	0	0	0	1	0	0	1	0

Table LIII.—Vertical Force Ranges (Unit 1γ). Number of Occurrences in Eleven Years.

Month.	From 0	12·5	25	37·5	50	62·5	75	100	125	150	175	200	250	500
	To 12·5	25	37·5	50	62·5	75	100	125	150	175	200	250	500	
January. . .	76	173	58	14	11	4	4	0	0	1	0	0	0	0
February . .	42	133	74	23	14	5	8	4	0	0	2	1	3	1
March. . . .	5	124	118	37	22	6	14	6	0	3	0	0	5	1
April	1	74	163	51	15	5	14	3	2	1	0	0	1	0
May.	0	43	171	67	33	10	5	2	2	2	1	2	3	0
June	0	76	169	48	14	12	5	2	1	0	1	1	1	0
July.	0	86	166	48	14	10	8	2	1	0	1	3	1	1
August . . .	2	111	158	46	11	1	5	2	1	1	0	1	1	1
September .	9	139	108	37	14	5	9	3	3	0	0	0	3	0
October. . .	22	168	91	25	17	8	5	4	1	0	0	0	0	0
November .	74	176	38	19	5	3	7	4	2	0	1	0	1	0
December .	125	142	43	14	9	2	3	0	2	0	0	0	1	0

The step for the six lowest classes is only $12{\cdot}5\gamma$, answering roughly to $2'{\cdot}5$ in D, or half the step employed in the corresponding tables in my previous paper. For the next five classes the step is 25γ. The twelfth class has a step of 50γ, the thirteenth of 250γ, while the last class includes the few ranges—none in D—which exceeded 500γ. It requires a large number of classes to show the distribution satisfactorily near the lower end of the scale. Towards the upper end of the scale, the occurrences are so few that the employment of a very large number of classes with small steps would have been a useless complication. It would, in fact, require a very much longer period of years to fix the exact law of incidence for ranges exceeding 200γ. To facilitate intercomparison, Table LIV. includes results for the whole year from the three elements. The 11 years, the four years representing sunspot maximum, and the three years representing sunspot minimum are treated separately. Table LIV. likewise gives results from the three elements for the three seasons, derived from the whole 11 years.

The results in Table LIV. are shown graphically in fig. 13. The number of days in each class was expressed as a percentage of the total number of days included in all the classes, and ordinates were drawn proportional to these percentages, due allowance being made for the difference between the steps in the earlier and later classes. The graphical representation was not carried beyond the 9th class, whose superior limit is 150γ, because the ordinates for the higher classes would have been too short to show satisfactorily, and the irregularities arising from insufficient length of period would have been too great. In all the curves the range of greatest frequency of occurrence is less than the arithmetic mean range. Also the range of most frequent occurrence is always greater for D than for H, and much larger for H than for V. On many days when the D and H curves show large irregular

TABLE LIV.—Ranges (Unit 1γ). Number of Occurrences.

Period or season.	Element.	From 0 To 12·5	12·5 25	25 37·5	37·5 50	50 62·5	62·5 75	75 100	100 125	125 150	150 175	175 200	200 250	250 500	500
Year. 11 years (4017 days)	D	2	144	321	559	801	767	836	315	117	69	37	21	28	0
	H	26	318	664	822	744	529	534	197	89	33	15	17	22	7
	V	356	1445	1357	429	179	71	87	32	15	8	6	8	20	4
Year. 1892 to 1895 (1461 days)	D	0	12	50	117	172	293	490	163	67	40	25	11	21	0
	H	0	31	147	211	278	265	293	116	51	22	9	14	19	5
	V	47	399	522	238	97	45	51	19	7	5	5	7	16	3
Year. 1890, 1899, 1900 (1095 days)	D	1	79	142	262	291	177	94	26	10	9	2	2	0	0
	H	19	158	299	296	167	76	54	15	8	2	0	1	0	0
	V	177	533	313	46	14	3	6	0	1	1	0	0	1	0
Winter (1322 days)	D	2	142	270	264	178	140	153	84	34	25	12	7	11	0
	H	26	276	345	238	157	104	84	43	30	6	3	3	5	2
	V	317	624	213	70	39	14	22	8	4	1	3	1	5	1
Equinox (1342 days)	D	0	2	40	169	292	266	312	136	60	30	22	3	10	0
	H	0	34	193	299	257	198	221	77	27	13	7	5	9	2
	V	37	505	480	150	68	24	42	16	6	4	0	0	9	1
Summer (1353 days)	D	0	0	11	126	331	361	371	95	23	14	3	11	7	0
	H	0	8	126	285	330	227	229	77	32	14	5	9	8	3
	V	2	316	664	209	72	33	23	8	5	3	3	7	6	2

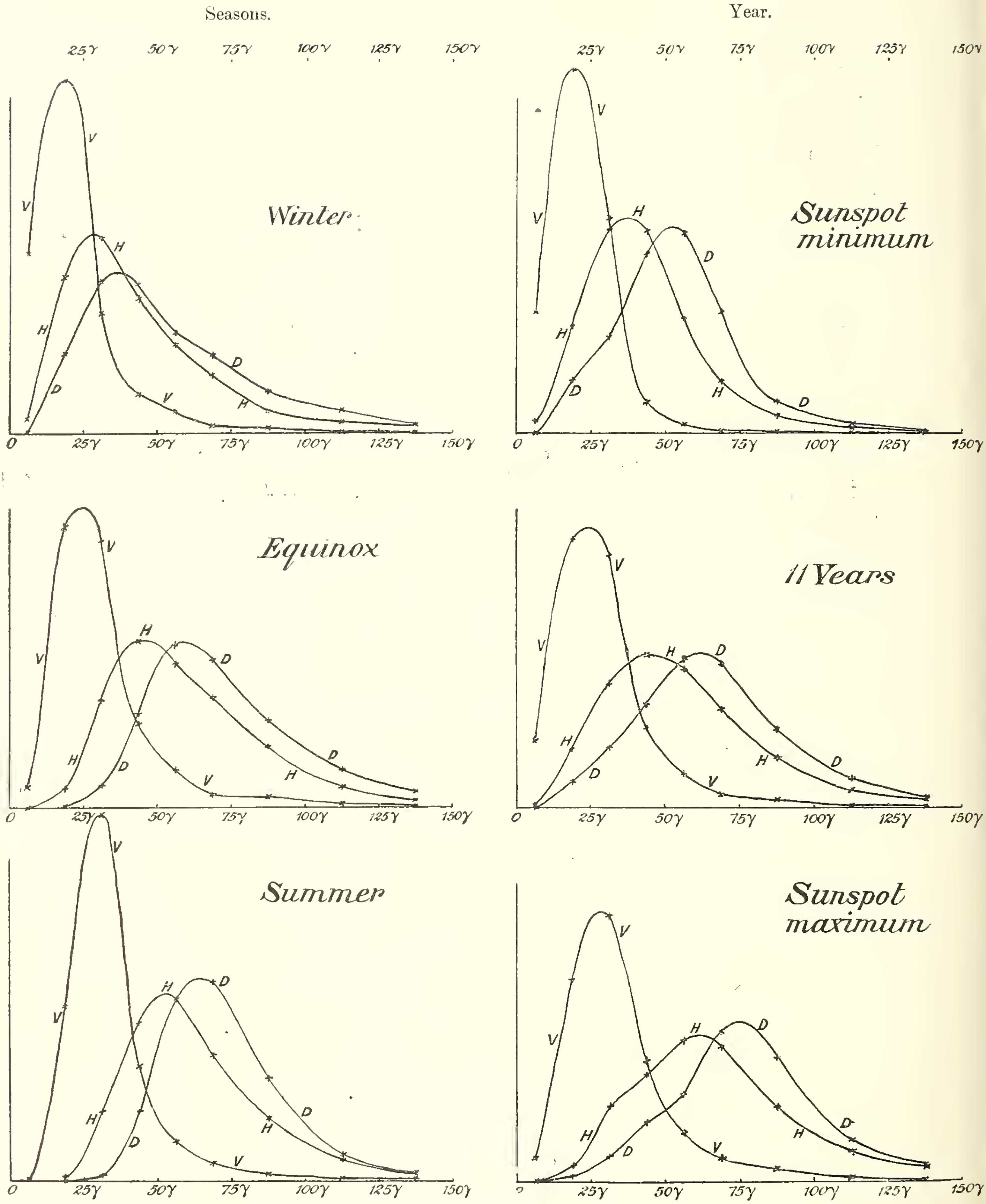

Fig. 13. Absolute daily ranges, frequency of occurrence.

oscillations, the V curve shows practically no trace of disturbance, or merely a slight exaggeration of the afternoon maximum. At times, however, V exhibits disturbances rivalling those in D and H. If we confine ourselves to days when the range exceeded 250γ, there were 24 occurrences in V as compared with 28 in D, and on 4 occasions the V range exceeded 500γ, while the largest D range observed was 457γ. During some of these very large disturbances the V trace—which has usually a gently rounded contour—showed large rapid oscillations just like the D and H traces.

The great majority of the largest storms occurred in 1892 or 1894. In the group of years of sunspot minimum a range as high as 250γ appeared only once in V, and on no single occasion in D or H.

There is a certain resemblance between the frequency curves for winter and for the sunspot minimum year, between those for equinox and for the average year, and again between those for summer and for the sunspot maximum year. The curves for the sunspot maximum year show a less smooth rise to the maximum ordinate than the others.

§ 30. Fig. 14 presents the range distribution data from a different point of view. Unit abscissa represents the arithmetic mean range for the element and season considered. Thus, in the case of the year from the 11 years, it represents 72·2γ in D, 60·7γ in H, and 32·9γ in V. This eliminates the effect of mere size, and so helps to bring out the degree of resemblance between the laws of distribution followed in different elements, or in the same element at different seasons. In the case of the whole year, the range of greatest frequency occurs very nearly at the same place—*i.e.*, bears very nearly the same ratio to the mean range—in the H and V curves; in D it answers to a decidedly larger abscissa.

In the case of H, the range of greatest frequency answers to a higher and higher fraction of the mean range as we pass from winter to equinox, and from equinox to summer. There is not much difference between the curves in fig. 14 answering to sunspot maximum and minimum, though the mean ranges are respectively 75·8γ and 43·9γ.

All the frequency curves have the general aspect of the ordinary diagram of intensity of visible and invisible radiation from a solid at high temperature. This, however, may mean no more than that the number of classes in which the ranges were grouped was too limited to show the existence of bands of reduced frequency or of no frequency. The existence of such bands, at least towards the side of the very high ranges, is by no means improbable, especially if storms should prove to have more than one origin.

For the careful measurement of the curves and the calculation of the hourly means I am indebted to various members, past and present, of the Kew Observatory staff. Amongst these I would particularly mention Messrs. G. BADDERLY and C. COOPER,

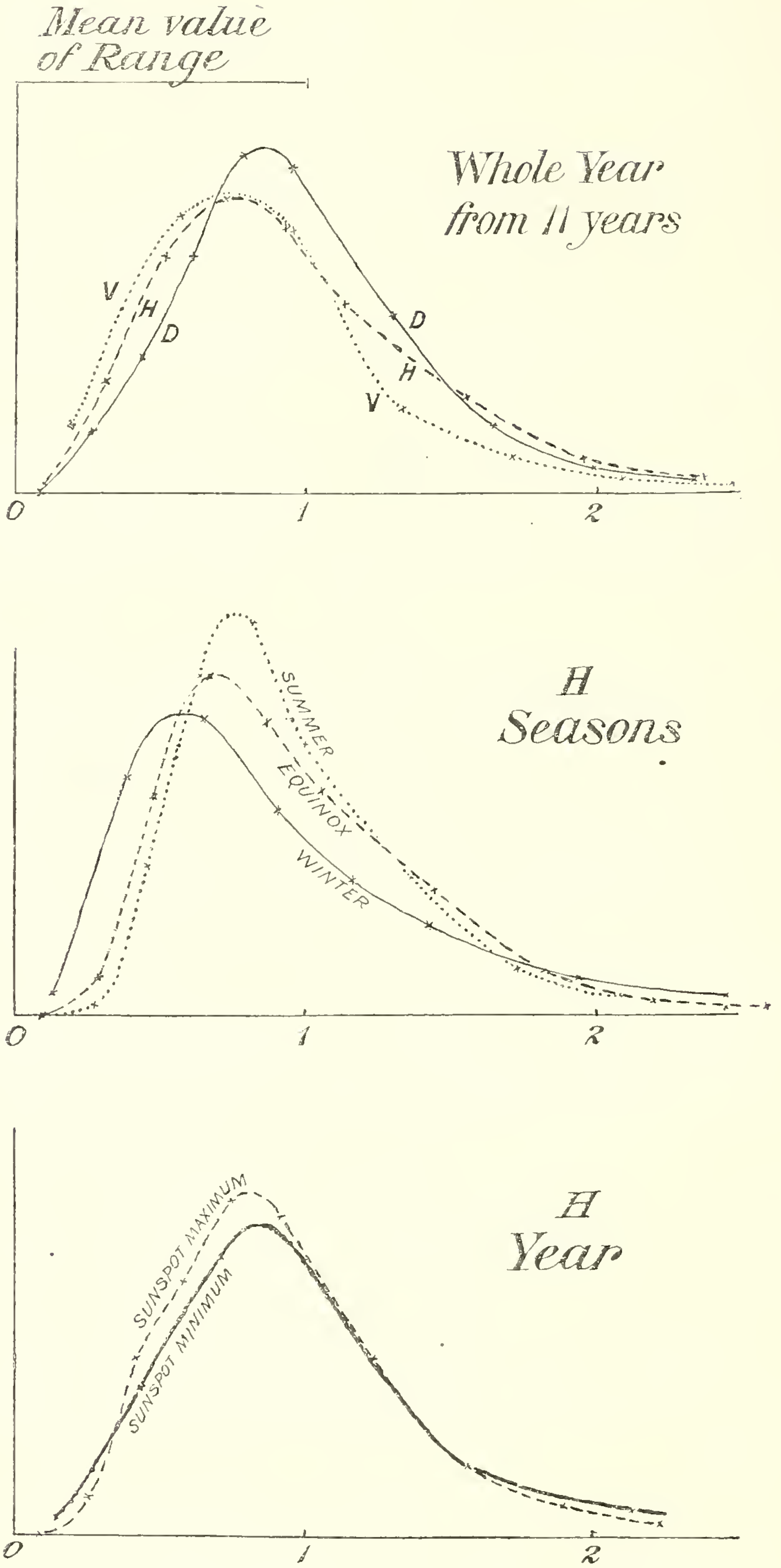

Fig. 14. Absolute daily ranges frequency of occurrence.

now of the National Physical Laboratory, and Mr. B. Francis, the present magnetic observer at Kew Observatory. During the eleven years whose records are mainly considered the magnetographs were under the charge of Mr. T. W. Baker, then Chief Assistant, who also took the great majority of the absolute observations. The homogeneousness of the material owes much to Mr. Baker. The expense of measuring the curves was defrayed mainly out of grants from the Government Grant Committee. The calculation of the diurnal inequalities, Fourier coefficients, and other arithmetical work has been mainly done in my leisure hours.

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S. CHAPMAN, M.A., D.Sc.,
FELLOW AND LECTURER OF TRINITY COLLEGE, CAMBRIDGE.

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Communicated by Sir JOSEPH LARMOR, *F.R.S.*

Received October 5,—Read November 18,—Revised December 1, 1915.

CONTENTS.

§ 1. INTRODUCTION.

THE kinetic theory of gases can be developed accurately only after the distribution of the molecular velocities has been determined. This was done by MAXWELL* in the case of a uniform gas, and by means of his well-known law of distribution the pressure and temperature can be precisely expressed in terms of the molecular data. His law does not suffice, however, for the investigation of diffusion, viscosity, or thermal conduction, since these occur only when the gas is *not* uniform in composition, mean velocity, or energy. An accurate theory of these phenomena must be based on the evaluation of the modified velocity-distribution function, a task which for many decades has constituted one of the classical unsolved problems of the kinetic theory.

---

* MAXWELL, 'Scientific Papers,' I., p. 377, II., p. 23. The proofs were unsatisfactory, and have been improved by BOLTZMANN, JEANS, and others.

[Published May 26, 1916.

In one special case, as MAXWELL found, the actual determination of this function proves to be unnecessary for the purpose mentioned; this is the case of a gas composed of molecules which are point centres of force varying inversely as the fifth power of the distance. The reasons for the peculiarity in this instance are analytical and not physical, and unfortunately for the simplicity of the mathematical theory of gases, MAXWELL'S results[*] for such a gas do not accord with the observed data of actual gases. This particular molecular model is therefore interesting chiefly on theoretical grounds, and it is important to develop the theory for molecules of other types, which may better represent the behaviour of real molecules.

Until recently no progress had been made towards the determination of the velocity-distribution function for a non-uniform gas, beyond a theorem by BOLTZMANN,[†] who proved that the function must satisfy a certain integral equation. In 1911, ENSKOG[‡] applied the method of solution by series to this equation; he determined the form of the function, but without evaluating its coefficients, and his numerical approximations proved far from satisfactory. In 1912, HILBERT[§] showed that if the molecules of the gas are rigid elastic spheres, BOLTZMANN'S equation may be transformed into a linear orthogonal integral equation of the second kind with a symmetrical kernel, and deduced the existence of a unique solution. LUNN[||] and PIDDUCK[¶] have since removed HILBERT'S restriction to a special type of molecule, and by means of the transformed equation PIDDUCK has worked out a numerical solution of a special problem on diffusion. These researches are of much importance and interest, especially from the logical standpoint of the pure mathematician. The use of BOLTZMANN'S equation, howevever, does not appear to be the best method of actually determining the formal solution; thus PIDDUCK states that the symmetrical kernel of the transformed equation shows no special properties in the case of Maxwellian molecules, and in the numerical solution it appears to be necessary to repeat all the calculations, which are very laborious, in every special case which is worked out.

In 1911, by the assumption of a simple form for the velocity-distribution function, I endeavoured to extend MAXWELL'S accurate theory of a gas to molecules of the most general kind compatible with spherical symmetry.[**] Subsequent acquaintance with ENSKOG'S work convinced me of the approximate nature of my results, and during the last few years I have given much thought to the determination of the general velocity-distribution function. By a method which is quite distinct from that based on

---

[*] MAXWELL, 'Scientific Papers,' II., p. 23. Molecules which are point centres of force varying inversely as the fifth power of the distance will, for the sake of brevity, be referred to as Maxwellian molecules.

[†] BOLTZMANN, 'Vorlesungen über Gastheorie,' I., p. 114.

[‡] ENSKOG, 'Physikalische Zeitschrift,' XII., 58, 1911.

[§] HILBERT, 'Math. Annalen,' 1912, or 'Linearen Integralgleichungen' (Teubner), 1912.

[||] LUNN, 'Bull. Amer. Math. Soc.,' 19, p. 455, 1913.

[¶] PIDDUCK, 'Proc. Lond. Math. Soc.,' (2), 15, p. 89, 1915; *cf.* p. 95 for the statement quoted.

[**] CHAPMAN, 'Phil. Trans.,' A, vol. 211, p. 433, 1911.

Boltzmann's equation, viz., by the use of the aggregate of the equations of transfer for certain infinite sequences of functions of the molecular velocities, an expression for the velocity-distribution function similar to that found by Enskog can be obtained, and general formulæ for the coefficients can be determined. The present paper contains the solution for a gas in which the mean velocity and the temperature vary from point to point, the results being worked out at all completely only for the case of a simple gas; in a later paper I hope to give the solution in the most general terms, so as to yield a complete theory of viscosity, thermal conduction, and diffusion in a composite gas formed of two kinds of spherically symmetrical molecules of any type.

The formulæ obtained by the present method lend themselves to numerical calculation, and are found to converge rapidly. The results for any particular molecular model can be calculated to any desired degree of accuracy; in this paper three special types of molecule have been considered, viz., point centres of force varying inversely as the n^{th} power of the distance, rigid elastic spheres, and rigid elastic attracting spheres. It is found that, for such molecules, the errors in the approximate formulæ for viscosity and thermal conduction which were given in my first paper do not exceed two or three per cent. at most. The detailed numerical results, and comparison with observed data, are given in §§ 10–12.

§ 2. Definition and Preliminary Consideration of the Problem.

The Nature of the Gas.

§ 2 (A). The gas contemplated in our calculations is monatomic and nearly perfect, "monatomic" implying nothing more than spherical symmetry of the molecules, while "nearly perfect" denotes a certain state as regards density and temperature; this state is such that the molecular paths are sensibly rectilinear for the majority of the time, being altered by mutual encounters, the duration of which is a very small fraction of the average interval *between* two encounters. In these circumstances the number and effect of encounters in which more than two molecules are simultaneously engaged is negligible in comparison with the number and effect of binary encounters.

The gas is supposed to be acted upon by external forces, and the variations of these forces, and of the density, mean velocity, and temperature of the gas, with regard to space and time, are small quantities of the first order at most. In the present paper the density of the gas is supposed such that the mean length of path of a molecule between collisions is small compared with the scale of the space-variation of the above quantities; the modifications of the theory in the case of highly rarefied gases, where the mean free path becomes large, will be dealt with in a future paper. As we are not interested in the mass motion or acceleration of the gas as a whole, but only in the small variations with regard to space and time, it is convenient to imagine that, by the addition of a suitable uniform motion and field of force to the whole gas, the mean velocity and acceleration at the particular point and time under consideration are reduced to zero, the velocity and acceleration at other points throughout the gas being small, though not actually zero.

Notation.

§ 2 (B) We shall denote the mass of a molecule by m, the number of molecules per unit volume at the point (x, y, z) by ν, the components of external force acting on a molecule at (x, y, z) by (X, Y, Z), the components of the velocity of a typical molecule by (u, v, w), and the components of the mean velocity of the gas at the point (x, y, z) by (u_0, v_0, w_0). The vector difference between the velocity of a typical molecule and the mean velocity (u_0, v_0, w_0) will be called the peculiar velocity of the molecule; we shall denote its components by $(\mathsf{U}, \mathsf{V}, \mathsf{W})$, so that

$$(1) \qquad \mathsf{U} = u - u_0, \quad \mathsf{V} = v - v_0, \quad \mathsf{W} = w - w_0.$$

The Distribution of Velocities.

§ 2 (C) The distribution of the molecular velocities may be specified by (u_0, v_0, w_0) together with a function $f(\mathsf{U}, \mathsf{V}, \mathsf{W})$, called the velocity-distribution function, which is defined by the following property: the number of molecules contained within a volume-element $dx\,dy\,dz$ about the point (x, y, z) which possess peculiar velocities whose three components lie respectively between $(\mathsf{U}, \mathsf{V}, \mathsf{W})$ and $(\mathsf{U}+d\mathsf{U}, \mathsf{V}+d\mathsf{V}, \mathsf{W}+d\mathsf{W})$ is

$$(2) \qquad \nu f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W}\, dx\, dy\, dz.$$

Besides being a function of U, V, W, f will depend on the mass m, the absolute temperature T and its space derivatives at the point (x, y, z), and on the space derivatives of (u_0, v_0, w_0), but not on the absolute magnitudes of the latter: for we may evidently impart an arbitrary additional velocity (u', v', w'), to the whole mass of gas without affecting the distribution of the *peculiar* velocities of the molecules at any point. It is therefore legitimate, and it will prove convenient, to suppose that, at the actual point under consideration, $u_0 = v_0 = w_0 = 0$; where u_0, v_0, w_0 occur in any expression which has to be differentiated, however, they must not be made equal to zero till after the differentiation has been performed.

In consequence of the definition of f and of U, V, W, f must satisfy the following equations:—

$$(3) \qquad \iiint f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W} = 1,$$

$$(4) \qquad \iiint \mathsf{U} f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W} = \iiint \mathsf{V} f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W}$$
$$= \iiint \mathsf{W} f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W} = 0.$$

If Q denotes any function of the velocity components (u, v, w) of a typical molecule, while $\overline{\mathrm{Q}}$ denotes its mean value at the point (x, y, z), we have

$$(5) \qquad \overline{\mathrm{Q}} = \iiint \mathrm{Q} f(\mathsf{U}, \mathsf{V}, \mathsf{W})\, d\mathsf{U}\, d\mathsf{V}\, d\mathsf{W},$$

in which, for purposes of integration, Q would be expressed in terms of $u_0+\mathsf{U}$, $v_0+\mathsf{V}$, $w_0+\mathsf{W}$ by (2). In the integrals (3) to (5), and elsewhere throughout the paper, integrations with respect to the velocity components are understood to be taken over all values of the variables, from $-\infty$ to $+\infty$.

The equations (4) may, in the notation just introduced, be expressed as follows:—

$$(6) \qquad \overline{\mathsf{U}} = \overline{\mathsf{V}} = \overline{\mathsf{W}} = 0.$$

The Velocity-distribution Function for a Uniform Gas.

§ 2 (D) When the gas is uniform, all the derivatives of T and of (u_0, v_0, w_0) are zero, and f must depend only on m, T, and $(\mathsf{U}, \mathsf{V}, \mathsf{W})$. It has, in fact, been shown by MAXWELL and others* that

$$(7) \qquad f = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)},$$

where

$$(8) \qquad \frac{1}{2h} = \mathrm{RT},$$

and R is the universal gas constant in the characteristic equation of a gas:

$$(9) \qquad p = \mathrm{R}\nu\mathrm{T}.$$

The Distribution Function for a Non-uniform Gas.

§ 2 (E) When the gas is slightly non-uniform, f will differ slightly from the value given by (7), which we shall denote by f_0: we may therefore write

$$(10) \quad f(\mathsf{U}, \mathsf{V}, \mathsf{W}) = f_0(\mathsf{U}, \mathsf{V}, \mathsf{W})\{1+\mathrm{F}(\mathsf{U}, \mathsf{V}, \mathsf{W})\} = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)}\{1+\mathrm{F}(\mathsf{U}, \mathsf{V}, \mathsf{W})\}.$$

The function F will be of the same order of magnitude as the variations of temperature and velocity in the gas; these space derivatives we shall regard as being of the first order, and as we shall neglect second order quantities throughout our work, no products of derivatives will occur in F. Hence, since F vanishes when the variations in the gas are zero, it must be a linear function of the space derivatives of T and (u_0, v_0, w_0), with no term independent of these derivatives. The coefficients will be functions of m, T, and U, V, W.

Clearly the form of F cannot depend upon any special choice of axes of reference (these are throughout taken to be mutually perpendicular), so that F is an invariant

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* *Cf.* JEANS' 'Dynamical Theory of Gases.'

with respect to any orthogonal transformation of the co-ordinate axes. This places some restriction upon the possible modes of occurrence in F of (U, V, W) and of the space derivatives of T and (u_0, v_0, w_0), though not, of course, on the scalar quantities m and T. It is easy to see that the most general invariant function of the quantities involved in F must be compounded of the following elementary invariants:—

$$(11) \qquad C^2 \equiv U^2+V^2+W^2,$$

$$(12), (13) \qquad S \equiv \frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}, \qquad \nabla^2 T \equiv \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) T,$$

$$(14) \qquad DT \equiv \left(U\frac{\partial}{\partial x}+V\frac{\partial}{\partial y}+W\frac{\partial}{\partial z}\right) T,$$

$$(15) \qquad S' \equiv U^2\frac{\partial u_0}{\partial x}+V^2\frac{\partial v_0}{\partial y}+W^2\frac{\partial w_0}{\partial z}+VW\left(\frac{\partial w_0}{\partial y}+\frac{\partial v_0}{\partial z}\right)+WU\left(\frac{\partial u_0}{\partial z}+\frac{\partial w_0}{\partial x}\right)+UV\left(\frac{\partial v_0}{\partial x}+\frac{\partial u_0}{\partial y}\right),$$

together with derivatives of the last four expressions formed by operating on them any number of times by the invariant differential operators ∇^2 and D, in the notation of (13) and (14).

[*January 15, 1916.*—Except in the case of highly rarefied gases, which were expressly excluded in § 2 (A), only the derivatives of the first *order* actually occur in F, to the present degree of accuracy. The reasons for this will perhaps be more clearly apparent after reading § 11, but the following considerations will elucidate the point. Whatever derivatives are contained in F must (§ 11) appear either in the equation of pressure or the equation of energy, so that, if the ordinary equations of viscosity and thermal conduction are to hold good, only the first-order space derivatives of temperature and mean velocity can be present; otherwise the ordinary coefficients of viscosity and conduction do not exist. In actual gases at normal densities the ordinary equations are shown by experiment to be valid; they fail, however, in highly rarefied gases because the terms in F which contain second-order differentials of T, u_0, v_0, w_0 are in this case comparable with those containing derivatives of the first order, as will be seen in detail in the future paper mentioned in § 2 (A). The coefficients of the first and second order derivatives respectively contain (λ/l) and $(\lambda/l)^2$, where λ is the mean free path of a molecule and l is comparable with the scale of length within which the temperature and mean velocity vary appreciably; except in rarefied gases $(\lambda/l)^2$ can be neglected in comparison with (λ/l). The same inferences can be made also (*cf.* § 6) from the equations of transfer of § 3.

For the present paper it is therefore sufficient (and it is convenient) to write down the following form of F forthwith:—

$$(16) \qquad F = \left(U\frac{\partial T}{\partial x}+V\frac{\partial T}{\partial y}+W\frac{\partial T}{\partial z}\right) P_1(C^2)+SP_2(C^2)+S'P_3(C^2),$$

this being the only way in which the first-order derivatives can occur in F, in order that F may be an invariant.

Here $P_1(C^2)$, $P_2(C^2)$, $P_3(C^2)$ denote certain undetermined functions of U, V, in which these variables appear only in the form $\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2$ or C^2. The first term of F is evidently of odd degree in U, V, W combined, and the second and third are of even degree; it is convenient to denote them by $O(\mathsf{U}, \mathsf{V}, \mathsf{W})$ and $E(\mathsf{U}, \mathsf{V}, \mathsf{W})$, when we wish to refer to the odd or even part of F separately.]

It is easy to see that, in a uniform gas, f_0 satisfies the necessary conditions (3), (4). In the non-uniform case these conditions require F to satisfy the equations

$$\iiint f_0 F \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = 0, \tag{17}$$

$$\iiint \mathsf{U} f_0 F \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = \iiint \mathsf{V} f_0 F \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = \iiint \mathsf{W} f_0 F \, d\mathsf{U} \, d\mathsf{V} \, d\mathsf{W} = 0. \tag{18}$$

Clearly the odd part $O(\mathsf{U}, \mathsf{V}, \mathsf{W})$ of F satisfies (17), and the even part $E(\mathsf{U}, \mathsf{V}, \mathsf{W})$ satisfies (18), but not *vice versâ*, so that these equations place certain restrictions on O and E.

§ 3. THE EQUATION OF TRANSFER OF MOLECULAR PROPERTIES.

§ 3 (A) The rate of change of $\nu\overline{Q}$, the aggregate value of $Q(u, v, w)$ per unit volume, may be analysed into three parts, viz., that due to molecular encounters (which we denote by ΔQ), that due to the passage of molecules in or out of the volume-element considered, and that due to the action of the external forces. The equation expressing this analysis may readily be shown* to be

$$\frac{\partial}{\partial t}(\nu\overline{Q}) = \Delta Q - \sum_{x, y, z}\left[\frac{\partial}{\partial x}(\nu\overline{uQ}) - \frac{\nu}{m} X \left(\overline{\frac{\partial Q}{\partial u}}\right)\right]. \tag{19}$$

We may define ΔQ by the statement that $(\Delta Q)\, dx\, dy\, dz\, dt$ is the change produced by molecular encounters during time dt in the sum ΣQ taken over all the molecules in the volume-element $dx\, dy\, dz$: evidently $\Sigma Q = \nu\overline{Q}\, dx\, dy\, dz$.

If in (19) we make Q equal to unity, in which case ΔQ is clearly zero, the equation becomes

$$\begin{aligned}\frac{\partial \nu}{\partial t} &= -\left(\frac{\partial \nu u_0}{\partial x} + \frac{\partial \nu v_0}{\partial y} + \frac{\partial \nu w_0}{\partial z}\right) \\ &= -\nu\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) - \left(u_0 \frac{\partial \nu}{\partial x} + v_0 \frac{\partial \nu}{\partial y} + w_0 \frac{\partial \nu}{\partial z}\right),\end{aligned}$$

which is the equation of continuity.

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* *Cf.* JEANS' 'Dynamical Theory of Gases.'

Except under the differential sign we shall write $u = \mathsf{U}$, $v = \mathsf{V}$, $w = \mathsf{W}$, since we are supposing that $u_0 = v_0 = w_0 = 0$ at the point (x, y, z). The last equation consequently reduces to

$$\frac{1}{\nu}\frac{\partial \nu}{\partial t} = -\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right). \tag{20}$$

In taking mean values of functions of U, V, W, as in (5), we shall neglect the part F in the velocity-distribution function f, in cases where the mean value is to be differentiated or multiplied by a small factor, since the resulting error is only of the second order.* Thus, in such cases, we shall write

$$\overline{\mathsf{U}^2\mathrm{C}^{2s}} = \tfrac{1}{3}\overline{\mathrm{C}^{2(s+1)}}, \quad \overline{\mathsf{U}^4\mathrm{C}^{2(s-1)}} = \tfrac{1}{5}\overline{\mathrm{C}^{2(s+1)}}, \quad \overline{\mathsf{V}^2\mathsf{W}^2\mathrm{C}^{2(s-1)}} = \tfrac{1}{15}\overline{\mathrm{C}^{2(s+1)}}, \tag{21}$$

$$\overline{\mathrm{C}^{2s}} = 1\,.\,3\,.\,5\,\ldots\,(2s+1)\,(2hm)^{-s}, \tag{22}$$

while, if either p, q or r is odd,

$$\overline{\mathsf{U}^p\mathsf{V}^q\mathsf{W}^r} = 0. \tag{23}$$

Since the equation of transfer involves derivatives of the first order only, it is sufficient, whenever the mean value of a function of u, v, w is to be differentiated, to expand it by TAYLOR'S theorem in terms of u_0, v_0, w_0, so far as the *first* degree only; if, then, the coefficient of u_0, v_0, w_0 is of type (23), the corresponding term may be omitted altogether.

Case I. $\mathrm{Q} = u\,(u^2+v^2+w^2)^s$.

§ 3 (B) When $\mathrm{Q} = u\,(u^2+v^2+w^2)^s$, according to the principles just laid down we have

$$\frac{\partial}{\partial x}(\nu\overline{u\mathrm{Q}}) = \frac{\partial}{\partial x}\,\nu\left(\overline{\mathsf{U}^2\mathrm{C}^{2s}} + 2u_0\overline{\mathsf{U}\mathrm{C}^{2s}} + 2s\overline{\mathsf{U}^2(u_0\mathsf{U}+v_0\mathsf{V}+w_0\mathsf{W})\,\mathrm{C}^{2(s-1)}} + \ldots\right)$$

$$= \tfrac{1}{3}\frac{\partial}{\partial x}\left(\nu\overline{\mathrm{C}^{2(s+1)}}\right) = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\frac{\partial}{\partial x}\,\nu\left(\frac{1}{2hm}\right)^{s+1}$$

$$= \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\left(\frac{1}{2hm}\right)^{s}\left\{\frac{1}{2hm}\frac{\partial \nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) + s\nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right)\right\},$$

$$\frac{\partial}{\partial y}(\nu\overline{v\mathrm{Q}}) = 0, \qquad \frac{\partial}{\partial z}(\nu\overline{w\mathrm{Q}}) = 0,$$

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* Except in gases of very low density.

neglecting in each case quantities of the second order. Since $\overline{\mathrm{Q}}$ is of the first order, to the same degree of accuracy as in the above equations, we have

$$\frac{\partial}{\partial t}(\nu\overline{\mathrm{Q}}) = 0.$$

Again, writing $u = \mathsf{U}$, $v = \mathsf{V}$, $w = \mathsf{W}$ after differentiation, we have

$$\left(\overline{\frac{\partial \mathrm{Q}}{\partial u}}\right) = \overline{\mathrm{C}^{2s}} + 2s\overline{\mathsf{U}^2\mathrm{C}^{2(s-1)}} = \tfrac{1}{3}(2s+3)\overline{\mathrm{C}^{2s}} = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\left(\frac{1}{2hm}\right)^s.$$

Here we have omitted $\overline{\mathsf{UV}\mathrm{C}^{2(s-1)}}$ and $\overline{\mathsf{UW}\mathrm{C}^{2(s-1)}}$, since when multiplied by X, which is of the first order, the result is of the second order, and hence negligible. Similarly

$$\left(\overline{\frac{\partial \mathrm{Q}}{\partial v}}\right) = 0, \qquad \left(\overline{\frac{\partial \mathrm{Q}}{\partial w}}\right) = 0.$$

The equation of transfer consequently takes the form

$$(24) \quad \Delta\mathsf{U}\mathrm{C}^{2s} = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\left(\frac{1}{2hm}\right)^s\left\{\frac{1}{2hm}\frac{\partial\nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) - \frac{\nu}{m}\mathrm{X} + s\nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right)\right\}.$$

When $s = 0$, this becomes

$$\Delta\mathsf{U} = \frac{1}{2hm}\frac{\partial\nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) - \frac{\nu}{m}\mathrm{X}.$$

Now $m\Delta\mathsf{U}$ is the rate of change of momentum per unit volume due to the molecular encounters, and, since action and re-action are equal and opposite, this change is zero. Hence we have, remembering that $(2h)^{-1} = \mathrm{RT} = p/\nu$,

$$(25) \qquad \nu\mathrm{X} = \frac{1}{2h}\frac{\partial\nu}{\partial x} + \nu\frac{\partial}{\partial x}\left(\frac{1}{2h}\right) = \frac{\partial}{\partial x}\left(\frac{\nu}{2h}\right) = \frac{\partial p}{\partial x},$$

which is one of the equations of pressure of the gas.

On substituting the value of X given by (25) into (24), the latter may be written

$$(26) \qquad \frac{(2hm)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+3)}\frac{3}{s\,\nu}\Delta\mathsf{U}\mathrm{C}^{2s} = \frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x},$$

where we have used the equation (*cf.* 8)

$$2hm\frac{\partial}{\partial x}\left(\frac{1}{2hm}\right) = \frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x}.$$

There are two equations similar to (26) giving $\Delta\mathsf{V}\mathrm{C}^{2s}$ and $\Delta\mathsf{W}\mathrm{C}^{2s}$ in terms of $\partial\mathrm{T}/\partial y$ and $\partial\mathrm{T}/\partial z$.

Case II. $Q = u^2(u^2+v^2+w^2)^s$.

§ 3 (C) Making approximations and reductions as in Case I., we have

$$\frac{\partial}{\partial t}(\nu\overline{Q}) = \frac{\partial}{\partial t}\left(\tfrac{1}{3}\nu\overline{C^{2(s+1)}}\right) = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\frac{\partial}{\partial t}\,\nu\left(\frac{1}{2hm}\right)^{s+1}$$

$$= \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{3}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\left\{\frac{1}{\nu}\frac{\partial\nu}{\partial t}+(s+1)\frac{1}{T}\frac{\partial T}{\partial t}\right\},$$

$$\frac{\partial}{\partial x}(\nu\overline{uQ}) = \frac{\partial}{\partial x}\,\nu\left\{\overline{U^3C^{2s}}+3u_0\overline{U^2C^{2s}}+2s\overline{U^3(u_0U+v_0V+w_0W)\,C^{2(s-1)}}+\ldots\right\}$$

$$= \frac{\partial}{\partial x}\,\nu u_0\left(\overline{C^{2(s+1)}}+\tfrac{2}{5}s\overline{C^{2(s+1)}}\right) = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+5)}{5}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial u_0}{\partial x},$$

$$\frac{\partial}{\partial y}(\nu\overline{vQ}) = \frac{\partial}{\partial y}\,\nu\left\{\overline{U^2VC^{2s}}+v_0\overline{U^2C^{2s}}+2s\overline{U^2V(u_0U+v_0V+w_0W)\,C^{2(s-1)}}+\ldots\right\}$$

$$= \frac{\partial}{\partial y}\,\nu v_0\left(\tfrac{1}{3}\overline{C^{2(s+1)}}+\tfrac{2}{15}s\overline{C^{2(s+1)}}\right) = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+5)}{15}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial v_0}{\partial y},$$

$$\frac{\partial}{\partial z}(\nu\overline{wQ}) = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+5)}{15}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\frac{\partial w_0}{\partial z}.$$

$$\overline{\left(\frac{\partial Q}{\partial u}\right)} = 2\overline{UC^{2s}}+2s\overline{U^3C^{2(s-1)}} = 0, \qquad \overline{\left(\frac{\partial Q}{\partial v}\right)} = 0, \qquad \overline{\left(\frac{\partial Q}{\partial w}\right)} = 0.$$

The equation of transfer may therefore be written

$$\Delta U^2C^{2s} = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{15}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\left[5\left\{\frac{1}{\nu}\frac{\partial\nu}{\partial t}+(s+1)\frac{1}{T}\frac{\partial T}{\partial t}\right\}\right.$$
$$\left.+(2s+5)\left(3\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)\right]. \tag{27}$$

When $s = 0$, this becomes

$$\Delta U^2 = \frac{\nu}{2hm}\left[\frac{1}{\nu}\frac{\partial\nu}{\partial t}+\frac{1}{T}\frac{\partial T}{\partial t}+3\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right].$$

If to this be added two similar equations giving ΔV^2 and ΔW^2, on the left-hand side we have $\Delta(U^2+V^2+W^2)$, which is the rate of change of molecular energy due to encounters; by the principle of conservation of energy this is zero, so that

$$3\left(\frac{1}{\nu}\frac{\partial\nu}{\partial t}+\frac{1}{T}\frac{\partial T}{\partial t}\right)+5\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right) = 0,$$

or, by (20),

$$\frac{1}{T}\frac{\partial T}{\partial t} = -\tfrac{2}{3}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right) = \tfrac{2}{3}\frac{1}{\nu}\frac{\partial\nu}{\partial t} = \tfrac{2}{3}\frac{1}{\rho}\frac{\partial\rho}{\partial t}. \tag{28}$$

On integration this gives $T\rho^{-2/3} = \text{constant}$, or, since $p = R\nu T$, it is equivalent to $p\rho^{-5/3} = \text{constant}$; this is the law of adiabatic expansion for a gas which possesses only translational energy.

Eliminating $\frac{1}{\nu}\frac{\partial \nu}{\partial t}$ and $\frac{1}{T}\frac{\partial T}{\partial t}$ from (27) by means of (20) and (28), we have

$$\Delta U^2C^{2s} = \frac{1\,.\,3\,.\,5\,\ldots\,(2s+3)}{15}\,\nu\left(\frac{1}{2hm}\right)^{s+1}\left[-\tfrac{5}{3}(2s+5)\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)\right.$$
$$\left.+(2s+5)\left(3\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)\right]$$
$$= \frac{1\,.\,3\,.\,5\,\ldots\,(2s+5)}{45}\,2\nu\left(\frac{1}{2hm}\right)^{s+1}\left(2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}\right), \tag{29}$$

or

$$\frac{(2hm)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+5)}\frac{45}{2\nu}\,\Delta U^2C^{2s} = 2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}. \tag{30}$$

By transformation of axes, or otherwise, we may deduce the equation

$$\frac{(2hm)^{s+1}}{1\,.\,3\,.\,5\,\ldots\,(2s+5)}\frac{45}{2\nu}\,\Delta 2VWC^{2s} = 3\left(\frac{\partial v_0}{\partial z}+\frac{\partial w_0}{\partial y}\right). \tag{31}$$

§ 4. THE EFFECT OF MOLECULAR ENCOUNTERS.

§ 4 (A) In this paper our primary concern is with simple gases containing molecules of one kind only; the difficulties are much enhanced when molecules of two kinds are present, especially as regards the equations of transfer, and the final determination of the coefficients of F when ΔQ has been calculated. These matters will be dealt with in a future paper, on diffusion and the general theory of composite gases. In the calculation of ΔQ, however, there is scarcely any advantage in making the restriction to one kind of molecule only, and it is convenient to carry out the calculation for a composite gas in order that the results may be quoted without repetition in the later, more general, investigation.

The notation of § 2 may be adapted to the case of a composite gas without further change than the addition of suffixes 1, 2 to denote to which group of molecules a symbol such as ν, m, U, V, W, f, F refers. The mean velocity of the two groups will be supposed the same, so that (u_0, v_0, w_0) is the same for both, either separately or together; similarly, their temperature or mean energy, and their relative densities (ν_1/ν_2) are supposed constant. All the remarks made concerning f and F hold both for f_1 and F_1, and f_2 and F_2, these being functions respectively of (U_1, V_1, W_1) and (U_2, V_2, W_2); they may each now be expected to involve $\nu_1 : \nu_2$ and $m_1 : m_2$ in addition to the quantities mentioned in § 2. A further important consideration which did not arise there is that f_1 and f_2, or F_1 and F_2 are *similar*, in the sense that either may be obtained from the other by interchanging the suffixes 1, 2.

Notation for an Encounter.

§ 4 (B) Before proceeding to the actual consideration of the dynamics of an encounter between two molecules m_1, m_2, it is convenient to explain the notation to be used. The symbols m_0, μ_1, μ_2, μ_{12}, and μ_{21} are defined as follows :—

(32) $$m_0 \equiv m_1+m_2,$$

(33) $$\mu_1 = m_1/m_0, \qquad \mu_2 = m_2/m_0,$$

(34) $$\mu_{12} = m_1/m_2 = \mu_1/\mu_2, \qquad \mu_{21} = m_2/m_1 = \mu_2/\mu_1,$$

so that

(35) $$\mu_1+\mu_2 = 1, \qquad \mu_1{}^2+\mu_2{}^2 = 1-2\mu_1\mu_2,$$

(36) $$\mu_{12}\mu_{21} = 1.$$

Velocities will be represented either by their x, y, z components or in vector notation. The components of the actual velocities of the molecules will be written $(\mathsf{U}, \mathsf{V}, \mathsf{W})$, while those of other velocities, such as the velocity of the mass-centre G, or the relative velocity, will be written $(\mathsf{X}, \mathsf{Y}, \mathsf{Z})$. The amplitude of a velocity will be denoted by C, and the vector itself by the same symbol in small type with a bar beneath, viz., $\underline{c}$.

The velocities of the molecules m_1, m_2, and of G will be distinguished by the respective suffixes 1, 2, 0, while the suffix R, similarly, will indicate reference to the molecular velocities *relative* to G or to one another. As regards time, square brackets enclosing a symbol, such as $[\mathsf{X}_0]$, $[\underline{c}_1]$. will indicate reference to some particular (arbitrary) instant during the encounter; a symbol without brackets but with an accent (′) will refer to any instant after the encounter,* while when there is neither bracket nor accent it will refer to any instant before the encounter.

Analysis of the Motions in an Encounter.

§ 4 (C) In the above notation the initial and final molecular velocities are respectively $\underline{c}_1$, $\underline{c}_2$ and $\underline{c}'_1$, $\underline{c}'_2$, or $(\mathsf{U}_1, \mathsf{V}_1\ \mathsf{W}_1)$, $(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)$ and $(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1)$, $(\mathsf{U}'_2, \mathsf{V}'_2, \mathsf{W}'_2)$; also

(37) $$C^2 = \mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2,$$

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* That is, any instant after the molecules have separated beyond the distance (which in actual gases is, at most, very small) at which their inter-action is appreciable; the words "before the encounter" are to be interpreted in a similar sense. In this sense the velocities of the molecules before and after the encounter are definite and constant.

where C, U, V, W all have the same suffix 1 or 2, with or without an accent (′). Similarly, the mass-centre G has the velocity $\underline{c}_0$ or (X_0, Y_0, Z_0), and since (by the principle of conservation of momentum) this remains invariable throughout the encounter,* we have

$$\underline{c}_0 = \mu_1\underline{c}_1+\mu_2\underline{c}_2 = \mu_1\underline{c}'_1+\mu_2\underline{c}'_2 = \mu_1[\underline{c}_1]+\mu_2[\underline{c}_2]. \tag{38}$$

or

$$\underline{c}_0 = \underline{c}'_0 = [\underline{c}_0].$$

Since, by (38),

$$m_1\{[\underline{c}_1]-[\underline{c}_0]\} = -m_2\{[\underline{c}_2]-[\underline{c}_0]\} = m_0\mu_1\mu_2\{[\underline{c}_1]-[\underline{c}_2]\} \equiv m_0(\mu_1\mu_2)^{1/2}[\underline{c}_R], \tag{39}$$

where $[\underline{c}_R]$ is *defined* by the equation

$$[\underline{c}_R] \equiv (\mu_1\mu_2)^{1/2}\{[\underline{c}_1]-[\underline{c}_2]\}, \tag{40}$$

we see that the momentum of the molecules, relative to G, is equal in magnitude but opposite in direction in the two cases, its value being $\pm m_0(\mu_1\mu_2)^{1/2}[\underline{c}_R]$. The relative velocity of the two molecules is, by (40), equal to $(\mu_1\mu_2)^{-1/2}[\underline{c}_R]$; this varies throughout the encounter, owing to the inter-action of the molecules; its initial and final values are given by

$$\underline{c}_R = (\mu_1\mu_2)^{-1/2}(\underline{c}_1-\underline{c}_2), \qquad \underline{c}'_R = (\mu_1\mu_2)^{-1/2}(\underline{c}'_1-\underline{c}'_2), \tag{41}$$

which are special cases of (40).

Equations (38), (41), and the reciprocal equations

$$\underline{c}_1 = \underline{c}_0+\mu_{21}^{1/2}\underline{c}_R \qquad c_2 = \underline{c}_0-\mu_{12}^{1/2}c_R, \tag{42}$$

$$\underline{c}'_1 = \underline{c}_0+\mu_{21}^{1/2}\underline{c}'_R \qquad \underline{c}'_2 = \underline{c}_0-\mu_{12}^{1/2}\underline{c}'_R, \tag{43}$$

indicate that $\underline{c}$, $\underline{c}_2$ or $\underline{c}'_1$, $\underline{c}'_2$ are equivalent to $\underline{c}_0$, $\underline{c}_R$ or $\underline{c}_0$, $\underline{c}'_R$, as specifications of the initial or final velocities of the molecules. Hence the problem of determining the final velocities of two molecules after an encounter, in terms of the initial velocities and whatever further independent variables are necessary to define the encounter, is equivalent to the determination of $\underline{c}'_R$ in terms of $\underline{c}_R$ and the variables of the encounter. Thus, in consequence of the invariability of $\underline{c}_0$, the velocity of the mass-centre, we need only consider the motion relative to G, *i.e.*, the motion referred to uniformly moving axes with G as origin.

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* We here suppose that the effect of the external forces during the brief interval of encounter is negligible; this is legitimate if the gas is "nearly perfect" (*cf.* § 2).

The Motion Relative to the Mass-centre.

§ 4 (D) Relative to these axes the molecules are initially moving along parallel lines with equal and opposite momenta $\pm m_0(\mu_1\mu_2)^{1/2}\underline{c}_R$, by (39). The plane containing these two lines is clearly the plane in which the inter-action and motion of the molecules will take place during the encounter. It is parallel to $\underline{c}_R$, but its orientation ϵ about this direction is independent of $\underline{c}_0$, $\underline{c}_R$, *i.e.*, it is one of the additional variables needed to specify the encounter, and, similarly, so also is the perpendicular distance p between the initial lines of relative motion. It is convenient to measure ϵ from the plane containing $\underline{c}_0$ and $\underline{c}_R$.

In the plane of relative motion so defined, the molecules describe orbits which are similar to one another (the origin G being the centre of similitude), and symmetrical about the line of apses (*i.e.*, points of closest approach). Each orbit has two asymptotes, one being the initial, the other the final line of motion; the distance between the pair of final asymptotes is clearly equal to that, p, between the initial asymptotes. The angle χ_{12} between the two asymptotes of either orbit measures the deflection of the relative motion due to the encounter; for molecules of given types it is a function of p and C_R[*] only, the nature of the function depending on the law of inter-action between a molecule m_1 and a molecule m_2. We shall find it convenient, for the sake of generality as well as of brevity, to retain χ_{12} as an unspecified function of p and C_R in our equations; the special properties of the molecules under consideration are, throughout our work, involved *only* through the dependence of χ_{12} on p and C_R.

It is easy to see that the *magnitude* of the relative velocity $(\mu_1\mu_2)^{-1/2}\underline{c}_R$ is unaltered by the encounter, *i.e.*,

$$C_R = C'_R: \tag{44}$$

for by the equation of energy we have

$$\tfrac{1}{2}(m_1C_1^2+m_2C_2^2) = \tfrac{1}{2}(m_1C_1'^2+m_2C_2'^2) = \tfrac{1}{2}m_0(C_0^2+C_R^2) = \tfrac{1}{2}m_0(C_0^2+C_R'^2) \tag{45}$$

by (42) and (43).

The Velocities in Spherical Polar Co-ordinates.

§ 4 (E) The above analysis of a molecular encounter may be made clearer by the following figure, in which x, y, z, c_0, c_R, c'_R are the points in which a unit sphere

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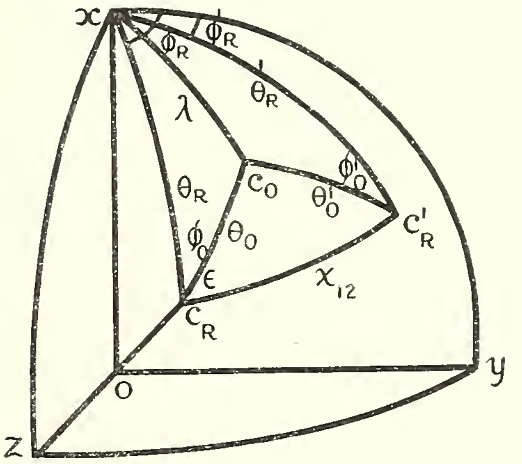
[*] That is, on p and on the *amplitude* C_R of the vector $\underline{c}_R$.

centred at O is cut by radii parallel respectively to the co-ordinate axes and to $\underline{c}_0$, $\underline{c}_R$, and $\underline{c}'_R$. Then we have

(45A) $$\epsilon = c_0 c_R c'_R, \qquad \chi_{12} = c_R O c'_R.$$



It is convenient also to use certain spherical polar co-ordinates, as follows, taking Ox, Oxy as initial line and plane for $\underline{c}_R$ and $\underline{c}'_R$, and Oc_R, Oc_Rx, or Oc'_R, Oc'_Rx for $\underline{c}_0$. Thus we write

(46) $$\theta_R = c_R O x, \qquad \theta'_R = c'_R O x, \qquad \theta_0 = c_0 O c_R, \qquad \theta'_0 = c_0 O c'_R, \qquad \lambda = c_0 O x,$$

(47) $$\phi_R = c_R x y, \qquad \phi'_R = c'_R x y, \qquad \phi_0 = c_0 c_R x, \qquad \phi'_0 = c_0 c'_R x.$$

Evidently we have

(48) $$\cos\theta'_0 = \cos\theta_0 \cos\chi_{12} + \sin\theta_0 \sin\chi_{12} \cos\epsilon,$$

(49) $$\cos\theta'_R = \cos\theta_R \cos\chi_{12} + \sin\theta_R \sin\chi_{12} \cos\overline{\epsilon+\phi_0},$$

(50) $$\cos\lambda = \cos\theta_0 \cos\theta_R + \sin\theta_0 \sin\theta_R \cos\phi_0,$$
$$= \cos\theta'_0 \cos\theta'_R + \sin\theta'_0 \sin\theta'_R \cos\phi'_0.$$

Expressions for the Velocities After an Encounter.

§ 4 (F) We have thus indicated how the final molecular velocities $\underline{c}'_1$, $\underline{c}'_2$ are to be determined (*cf.* 43) in terms of the initial velocities $\underline{c}_1$, $\underline{c}_2$ or $\underline{c}_0$, $\underline{c}_R$ together with p and ϵ (these being the eight independent variables of an encounter). This has been done by showing how $\underline{c}'_R$ depends upon $\underline{c}_R$, p and ϵ; it has in fact been shown that the spherical polar co-ordinates of $\underline{c}'_R$, referred to $\underline{c}_R$ and the plane $\underline{c}_0$, $\underline{c}_R$ as initial line and plane, are C_R, χ_{12} (a function of p and C_R) and ϵ. Hence we may at once write down the expressions for the initial and final velocities and velocity components in terms of $\underline{c}_0$, $\underline{c}_R$, p and ϵ, as follows:—

$$(51)\quad \mu_1 C_1^{\,2} = \Theta_{12}(\cos\theta_0),\quad \mu_2 C_2^{\,2} = \Theta_{21}(\cos\theta_0),\quad \mu_1 C'^{\,2}_1 = \Theta_{12}(\cos\theta'_0),\quad \mu_2 C'^{\,2}_2 = \Theta_{21}(\cos\theta'_0),$$

$$(52)\quad \begin{cases} \mu_1^{1/2}\mathsf{U}_1 = \mu_1^{1/2}C_0\cos\lambda + \mu_2^{1/2}C_R\cos\theta_R, & \mu_2^{1/2}\mathsf{U}_2 = \mu_2^{1/2}C_0\cos\lambda - \mu_1^{1/2}C_R\cos\theta_R, \\ \mu_1^{1/2}\mathsf{U}'_1 = \mu_1^{1/2}C_0\cos\lambda + \mu_2^{1/2}C_R\cos\theta'_R, & \mu_2^{1/2}\mathsf{U}'_2 = \mu_2^{1/2}C_0\cos\lambda - \mu_1^{1/2}C_R\cos\theta'_R. \end{cases}$$

where we have adopted the convenient notation* defined by

$$(53)\quad \begin{cases} \Theta_{12}(\cos\theta) \equiv \mu_1 C_0^{\,2} + \mu_2 C_R^{\,2} + 2(\mu_1\mu_2)^{1/2} C_0 C_R \cos\theta, \\ \Theta_{21}(\cos\theta) \equiv \mu_2 C_0^{\,2} + \mu_1 C_R^{\,2} - 2(\mu_1\mu_2)^{1/2} C_0 C_R \cos\theta. \end{cases}$$

Equations (51) to (53) are merely particular cases of (42), (43), expressed in terms of amplitudes (51, 53) and of x-components (52). The latter might also have been written in terms of the components of C_0 and C_R, as, for example,

$$(54)\qquad \mathsf{U}'_1 = \mathsf{X}_0 + \mu_{21}^{1/2}\mathsf{X}'_R = \mathsf{X}_0 + \mu_{21}^{1/2}\{\mathsf{X}_R\cos\chi_{12} + (\mathsf{Y}_R^{\,2} + \mathsf{Z}_R^{\,2})^{1/2}\sin\chi_{12}\cos(\epsilon+\phi_0)\},$$

by (49), writing $(\mathsf{X}_0, \mathsf{Y}_0, \mathsf{Z}_0)$, $(\mathsf{X}_R, \mathsf{Y}_R, \mathsf{Z}_R)$, $(\mathsf{X}'_R, \mathsf{Y}'_R, \mathsf{Z}_R')$, for the components of $\underline{c}_0$, $\underline{c}_R$ $\underline{c}'_R$. Equations similar to (53), (54) may easily be written down also for the y and z components of the velocities.

The Dependence of U'_1, V'_1, W'_1 *on* χ_{12}.

§ 4 (G) From (51) and (54) it is clear that any function $Q_1(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1)$ of U'_1, V'_1, W' is a function of U_1, V_1, W_1, U_2, V_2, W_2, p and ϵ, or of U_1, V_1, W_1, U_2, V_2, W_2, χ_{12} and ϵ, since p is involved only through χ_{12} (though χ_{12} is not entirely independent of the preceding six variables, since it depends upon C_R). If $Q_1(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1)$ be regarded as a function of χ_{12}, when χ_{12} is made equal to zero it reduces to $Q_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)$ simply: this may be seen either from (51)–(54) or, still more readily, from the figure on p. 293, since when $\chi_{12} = 0$, $\underline{c}'_R$ becomes identical with $\underline{c}_R$, and hence by (42), (43), so also does $\underline{c}'_1$ with $\underline{c}_1$.

Transformation of Co-ordinates.

§ 4 (H) In § 5 we require the Jacobian of transformation

$$J \equiv \frac{\partial(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1, \mathsf{U}'_2, \mathsf{V}'_2, \mathsf{W}'_2)}{\partial(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1, \mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)}$$

between the initial and final velocity components, p and ϵ being constant. Since the motion during an encounter is reversible, the relation between the two sets of velocity

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* In § 7, for the sake of brevity, we shall write Θ_{12}, Θ_{21}, Θ'_{12}, Θ'_{21} respectively for $\Theta_{12}(\cos\theta_0)$, $\Theta_{21}(\cos\theta_0)$, $\Theta_{12}(\cos\theta'_0)$, and $\Theta_{21}(\cos\theta'_0)$.

components is reciprocal, so that $J = \pm 1$. It may readily be seen that the positive sign is the correct one, by considering a particular case of variation, say $dU_1 = dU_2 = dU$, $dV_1 = dV_2 = dV$, $dW_1 = dW_2 = dW$. This is equivalent to the addition of a small velocity (dU, dV, dW) to the whole system; obviously this will reappear in the final velocities, so that also $dU'_1 = dU'_2 = dU$, $dV'_1 = dV'_2 = dV$, $dW'_1 = dW'_2 = dW$. In this case, and therefore always, we have $J = 1$, so that

$$dU'_1\, dV'_1\, dW'_1\, dU'_2\, dV'_2\, dW'_2 = dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2. \tag{55}$$

With a little more trouble this might also be proved analytically from the equations of this section.

From the component equations corresponding to (42), (43), *i.e.*, from

$$\left\{\begin{array}{lll} U_1 = X_0 + \mu_{21}{}^{1/2} X_R, & V_1 = Y_0 + \mu_{21}{}^{1/2} Y_R, & W_1 = Z_0 + \mu_{21}{}^{1/2} Z_R, \\ U_2 = X_0 - \mu_{12}{}^{1/2} X_R, & V_2 = Y_0 - \mu_{12}{}^{1/2} Y_R, & W_2 = Z_0 - \mu_{12}{}^{1/2} Z_R, \end{array}\right. \tag{56}$$

$$C_0{}^2 = X_0{}^2 + Y_0{}^2 + Z_0{}^2, \qquad C_R{}^2 = X_R{}^2 + Y_R{}^2 + Z_R{}^2, \tag{57}$$

it is easy to prove that

$$\frac{\partial\,(U_1, V_1, W_1, U_2, V_2, W_2)}{\partial\,(X_0, Y_0, Z_0, X_R, Y_R, Z_R)} = -(\mu_1\mu_2)^{-3/2}. \tag{58}$$

Hence, by further transformation to polar co-ordinates, we have

$$\begin{aligned} dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2 &= -(\mu_1\mu_2)^{-3/2}\, dX_0\, dY_0\, dZ_0\, dX_R\, dY_R\, dZ_R \\ &= -(\mu_1\mu_2)^{-3/2}\, C_0{}^2 C_R{}^2\, dC_0\, dC_R\, d\cos\theta_0\, d\cos\theta_R\, d\phi_0\, d\phi_R. \end{aligned} \tag{59}$$

Since $dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2$ is essentially positive, the negative sign on the right of (59) must be made positive, if the limits of C, $\cos\theta$, and ϕ in each case are taken as 0 to $+\infty$, -1 to $+1$, and 0 to 2π respectively; it may readily be seen that the negative sign corresponds to reversed limits of integration of one of the variables $\cos\theta$.

§ 5. The General Expression for ΔQ_1.

Definition of $\Delta_{11}Q_1$ and $\Delta_{12}Q_1$.

§ 5 (A) The rate of change of $\nu_1\overline{Q_1}$ due to molecular encounters, *i.e.*, ΔQ_1, may be divided into the two parts $\Delta_{11}Q_1$, $\Delta_{12}Q_1$ due respectively to the encounters of the molecules m_1 among themselves, and those with molecules m_2. Thus

$$\Delta Q_1 = \Delta_{11}Q_1 + \Delta_{12}Q_1. \tag{60}$$

We shall chiefly consider $\Delta_{12}Q_1$, whence $\Delta_{11}Q_1$ may be obtained by changing the suffix 2 into 1 throughout.

The Expression for $\Delta_{12}Q_1$.

§ 5 (B) The number of molecules m_1 having velocity components lying between the limits (U_1, V_1, W_1) and $(U_1+dU_1, V_1+dV_1, W_1+dW_1)$ is, by our definition of $f_1(U_1, V_1, W_1)$, equal to

$$\nu_1 f_1(U_1, V_1, W_1)\, dU_1\, dV_1\, dW_1$$

per unit volume. The number of encounters in time dt of any *one* of these, with a molecule m_2 having velocity components lying between the limits (U_2, V_2, W_2) and $(U_2+dU_2, V_2+dV_2, W_2+dW_2)$, the variables p, ϵ of the encounter lying between p and $p+dp$, ϵ and $\epsilon+d\epsilon$, is equal to the number of such molecules m_2 contained within a small cylinder of length $(\mu_1\mu_2)^{-1/2}C_R\, dt$ and of sectional area $p\, dp\, d\epsilon$, *i.e.*, to

$$\nu_2(\mu_1\mu_2)^{-1/2} f_2(U_2, V_2, W_2)\, C_R p\, dp\, d\epsilon\, dU_2\, dV_2\, dW_2\, dt.$$

Thus the total number of encounters of the above type, per unit volume per unit time, is

$$(61) \qquad \nu_1\nu_2(\mu_1\mu_2)^{-1/2} f_1(U_1, V_1, W_1)\, f_2(U_2, V_2, W_2)\, C_R p\, dp\, d\epsilon\, dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2.$$

At each such encounter the change in the value of $Q_1(U_1, V_1, W_1)$ is clearly

$$(62) \qquad Q_1(U'_1, V'_1, W'_1) - Q_1(U_1, V_1, W_1),$$

or $Q'_1 - Q_1$, as we shall write it for brevity.

We shall include the effect of all possible encounters per unit volume per unit time if we integrate the product of (61) and (62) over all values of ϵ (0 to 2π), p (0 to ∞) and (U_1, V_1, W_1), (U_2, V_2, W_2) (each from $-\infty$ to $+\infty$). Such an integration will include encounters which are not binary, but our postulate that the gas is nearly perfect (§ 2) implies that our integral would be altered only inappreciably if the upper limit of integration for p were not infinity but equal to the very small distance at which two molecules cease to exercise any appreciable inter-action. Hence, throughout this paper, where no limits of integration are specified, it is to be understood that they have the above values. Thus we have

$$(63) \quad \Delta_{12}Q_1 = \nu_1\nu_2(\mu_1\mu_2)^{-1/2}\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int\!\!\int (Q'_1 - Q_1) f_1 f_2 C_R p\, dp\, d\epsilon\, dU_1\, dV_1\, dW_1\, dU_2\, dV_2\, dW_2.$$

The term $f_1 f_2$ in the integrand may be written

$$(64) \qquad \left(\frac{hm_1}{\pi}\right)^{3/2}\left(\frac{hm_2}{\pi}\right)^{3/2} e^{-h(m_1C_1^2+m_2C_2^2)}\left\{1 + F_1(U_1, V_1, W_1) + F_2(U_2, V_2, W_2)\right\}$$

$$= (\mu_1\mu_2)^{3/2}\left(\frac{hm_0}{\pi}\right)^3 e^{-hm_0(C_0^2+C_R^2)}(1 + F_1 + F_2),$$

where, in the first line, we have neglected F_1F_2, which is a second-order quantity, while in the second line we have made use of (45).

The unit term in $(1+F_1+F_2)$ *may be omitted.*

§ 5 (C) It is easy to show that the part of (63) which arises from the unit term of $(1+F_1+F_2)$ in (64) is zero. For it may be written in the form

$$\iint \phi\nu_1\nu_2\mu_1\mu_2\,(hm_0/\pi)^3\,C_R\,p\,dp\,d\epsilon,$$

where

$$\phi \equiv \iiiint\!\!\iint \{Q_1(U'_1, V'_1, W'_1) - Q_1(U_1, V_1, W_1)\}\,e^{-hm_0(C_0^2+C_R^2)}\,dU_1\,dV_1\,dW_1\,dU_2\,dV_2\,dW_2.$$

Now by (45) and (55) the latter is equal to

$$(65)\qquad \iiiint\!\!\iint Q_1(U'_1, V'_1, W'_1)\,e^{-h(m_1C'^2_1+m_2C'^2_2)}\,dU'_1\,dV'_1\,dW'_1\,dU'_2\,dV'_2\,dW'_2$$
$$-\iiiint\!\!\iint Q_1(U_1, V_1, W_1)\,e^{-h(m_1C_1^2+m_2C_2^2)}\,dU_1\,dV_1\,dW_1\,dU_2\,dV_2\,dW_2.$$

But the latter two integrals are equal, since they are definite integrals differing only in the symbols used to denote the variables. Hence (65) is zero, and the unit term in $(1+F_1+F_2)$ may be omitted from $\Delta_{12}Q_1$.

The same result can be seen also in another way: the part of $\Delta_{12}Q_1$ under consideration is that obtained by putting $F_1 = F_2 = 0$ in f_1f_2, *i.e.*, it is equal to the value of $\Delta_{12}Q_1$ in a uniform gas. In a uniform gas, however, as we may see from the general equation of transfer (19), $\Delta_{11}Q_1 = \Delta_{12}Q_1 = 0$, whence the result follows at once.

If $Q(U, V, W)$ *is of odd degree, the even part of* $F(U, V, W)$ *contributes nothing to* $\Delta_{12}Q$, *and* vice versâ.

§ 5 (D) We may now, therefore, write $\Delta_{12}Q_1$ in the following form, transforming the variables (U_1, V_1, W_1), (U_2, V_2, W_2) to (X_0, Y_0, Z_0), (X_R, Y_R, Z_R), by (56), (58).

$$(66)\quad \Delta_{12}Q_1 = \nu_1\nu_2\mu_1\mu_2\left(\frac{hm_0}{\pi}\right)^3$$
$$\iiiint\!\!\iiiint (Q'_1-Q_1)\,e^{-hm_0(C_0^2+C_R^2)}\,(F_1+F_2)\,C_R p\,dp\,d\epsilon\,dU_1\,dV_1\,dW_1\,dU_2\,dV_2\,dW_2$$
$$= \nu_1\nu_2(\mu_1\mu_1)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3$$
$$\iiiint\!\!\iiiint (Q'_1-Q_1)\,e^{-hm_0(C_0^2+C_R^2)}\,(F_1+F_2)\,C_R p\,dp\,d\epsilon\,dX_0\,dY_0\,dZ_0\,dX_R\,dY_R\,dZ_R.$$

We here suppose the functions $Q(U, V, W)$ and $F(U, V, W)$ expressed in terms of the new variables and (in the case of Q'_1) of ϵ and χ_{12} (or p). We are concerned both as regards Q and F only with terms which are integral in the variables U, V, W; in reckoning their degree we shall make no distinction between U_1 and U_2, &c., or between X_0 and X_R,[*] &c. Then since the equations of transformation (56) are linear, any term $\mathsf{U}_1{}^l\mathsf{V}_1{}^m\mathsf{W}_1{}^n\mathsf{U}_2{}^p\mathsf{V}_2{}^q\mathsf{W}_2{}^r$ in $Q_1\,(F_1+F_2)$ transforms into the sum of a number of terms $\mathsf{X}_0{}^a\mathsf{Y}_0{}^b\mathsf{Z}_0{}^c\mathsf{X}_R{}^d\mathsf{Y}_R{}^e\mathsf{Z}_R{}^f$ such that

$$l+p = a+d, \qquad m+q = b+e, \qquad n+r = c+f.$$

This is not true in the case of $Q'_1\,(F_1+F_2)$, since (by 54) U'_1, V'_1, W'_1 are not rational functions of the variables X, Y, Z, but it *is* true of $(F_1+F_2)\int Q'_1\,d\epsilon$, since the integration with respect to ϵ causes all the irrational terms in Q'_1 to disappear.[†] This may be proved quite generally, but it will be sufficient here to indicate the proof for the case $Q_1 = \mathsf{U}_1C_1{}^{2s}$, s being any positive integer. We may write

$$Q'_1 = \mathsf{U}'_1C'_1{}^{2s} = (\mathsf{X}+aC_R\sin\theta_R\cos\overline{\epsilon+\phi_0})\,(C^2+2aC_0C_R\sin\theta_0\cos\epsilon)^s,$$

where

$$a = \mu_{21}{}^{1/2}\sin\chi_{12}, \qquad \mathsf{X} = \mathsf{X}_0+\mu_{21}{}^{1/2}\mathsf{X}_R\cos\chi_{12},$$

$$C'^2 = C_0{}^2+\mu_{21}C_R{}^2+2\mu_{21}{}^{1/2}\,(\mathsf{X}_0\mathsf{X}_R+\mathsf{Y}_0\mathsf{Y}_R+\mathsf{Z}_0\mathsf{Z}_R)\cos\chi_{12},$$

so that X is of the first degree in X_0 or X_R, and C^2 is of even degree in the variables $(\mathsf{X}_0, \mathsf{X}_R)$, $(\mathsf{Y}_0, \mathsf{Y}_R)$, $(\mathsf{Z}_0, \mathsf{Z}_R)$. The only terms in Q'_1 which do not vanish on integration with respect to ϵ are of the form

$$\mathsf{X}\,\{{}_sC_{2p}\,(C'^2)^{s-2p}\,(2aC_0C_R\sin\theta_0\cos\epsilon)^{2p}\}$$

or

$$(C_0C_R{}^2\sin\theta_0\sin\theta_R\cos^{2p+1}\epsilon\cos\overline{\epsilon+\phi_0})\,\{2a^2{}_sC_{2p+1}\,(C'^2)^{s-2p-1}\,(2aC_0C_R\sin\theta_0)^{2p}\}.$$

Now we have

$$(C_0C_R\sin\theta_0)^2 = C_0{}^2C_R{}^2\,(1-\cos^2\theta_0) = \{C_0{}^2C_R{}^2-(\mathsf{X}_0\mathsf{X}_R+\mathsf{Y}_0\mathsf{Y}_R+\mathsf{Z}_0\mathsf{Z}_R)^2\},$$

which is an even function of X, Y, Z, and can be included under the symbol C^2. Thus, on integration with respect to ϵ, the above expressions become (apart from a factor not involving X, Y, Z explicitly)

$$\mathsf{X}C'^{2s}, \quad (C_0C_R{}^2\sin\theta_0\sin\theta_R\cos\phi_0)\,C'^{2(s-1)}$$

and by (50) the latter may be written

$$C_0C_R{}^2\,(\cos\lambda-\cos\theta_0\cos\theta_R)\,C'^{2(s-1)} = [\mathsf{X}_0C_R{}^2-\mathsf{X}_R\,(\mathsf{X}_0\mathsf{X}_R+\mathsf{Y}_0\mathsf{Y}_R+\mathsf{Z}_0\mathsf{Z}_R)]\,C'^{2(s-1)}.$$

Both these expressions, and consequently $\int Q_1\,(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1)\,d\epsilon$ as a whole, are of the form $\mathsf{X}C^{2s}$ in the sense above defined. Similarly it may be shown that $\int \mathsf{U}'_1{}^2C'_1{}^{2s}\,d\epsilon$ is even in all three variables $(\mathsf{X}_0, \mathsf{X}_R)$, $(\mathsf{Y}_0, \mathsf{Y}_R)$, $(\mathsf{Z}_0, \mathsf{Z}_R)$.

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[*] So that, for instance, $\mathsf{x}_0{}^2$, $\mathsf{x}_0\mathsf{x}_R$ and $\mathsf{x}_R{}^2$ will all be regarded as even functions of x.

[†] The *explicit* occurrence of x, y, z in $\int Q'_1\,d\epsilon$ is here referred to; the latter may involve C_R irrationally through χ_{12}.

In the integrand of (66), the exponential term and C_R (whether occurring as an explicit factor or implicitly in χ_{12}) are even functions of X, Y, Z. Hence a term such as $\mathsf{X}_0{}^a\mathsf{Y}_0{}^b\mathsf{Z}_0{}^c\mathsf{X}_R{}^d\mathsf{Y}_R{}^e\mathsf{Z}_R{}^f$ in $\int(Q'_1-Q_1)(F_1+F_2)\,d\epsilon$ will contribute nothing to $\Delta_{12}Q_1$ unless a, b, c, d, e, f and *à fortiori* $a+d$, $b+e$, $c+f$ are all separately even. In view of what has been proved above, therefore, it appears that in $Q(\mathsf{U}, \mathsf{V}, \mathsf{W})\,F(\mathsf{U}, \mathsf{V}, \mathsf{W})$ only the terms which are even in U, V, W separately contribute anything to $\Delta_{12}Q_1$. Hence if Q is odd in U, only the part of F which is likewise odd in U need be considered, while if it is even in U, only the even part of F need be considered.

Introduction of $I_1(\chi_{12})$.

§ 5 (E) We now make the final transformation of $\Delta_{12}Q_1$ by adopting polar co-ordinates in place of $(\mathsf{X}_0, \mathsf{Y}_0, \mathsf{Z}_0)$, $(\mathsf{X}_R, \mathsf{Y}_R, \mathsf{Z}_R)$, as follows :—

$$(67)\qquad \Delta_{12}Q_1 = \nu_1\nu_2(\mu_1\mu_2)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3\int\int\int e^{-hm_0(C_0{}^2+C_R{}^2)}\{I_1(\chi_{12})-I_1(0)\}\,C_0{}^2C_R{}^3p\,dp\,dC_0\,dC_R,$$

where

$$(68)\ I_1(\chi_{12}) = \int\int\int\int\int Q_1(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1)\{F_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)+F_2(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)\}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_R\,d\phi_0\,d\phi_R,$$

$$(69)\ I_1(0) = \int\int\int\int\int Q_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)\{F_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)+F_2(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)\}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_R\,d\phi_0\,d\phi_R.$$

Evidently (*cf.* § 4 (G)) the latter is obtained when χ_{12} is made zero in $I_1(\chi_{12})$, since χ_{12} is not concerned in the integrations of (68), (69), being a function of p and C_R only, while when $\chi_{12} = 0$ we have $Q_1(\mathsf{U}'_1, \mathsf{V}'_1, \mathsf{W}'_1) = Q_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)$. Hence, in calculating $\Delta_{12}Q_1$ we shall concern ourselves only with $I_1(\chi_{12})$ until we come to the integration with respect to p, C_R, C_0. In so doing we shall, from the outset, omit from $F(\mathsf{U}, \mathsf{V}, \mathsf{W})$ those parts which, in accordance with § 5 (D), contribute nothing to the final result.

§ 6. THE FORM OF THE FUNCTION $F(\mathsf{U}, \mathsf{V}, \mathsf{W})$.

The two special forms of Q_1 which we consider are $\mathsf{U}_1{}^2C_1{}^{2s}$ and $\mathsf{U}_1C_1{}^{2s}$; the only parts of $F(\mathsf{U}, \mathsf{V}, \mathsf{W})$ which are relevant in these cases are respectively the part of E_1+E_2, which is even in V and W_2, and O_1+O_2; the notation here used is that of § 2 (E), p. 283. From (26) and (30) we see that $\Delta\mathsf{U}_1C_1{}^{2s}$ involves the space derivatives of mean properties of the gas only in the form $\frac{1}{T}\frac{\partial T}{\partial x}$, while $\Delta\mathsf{U}_1{}^2C_1{}^{2s}$ similarly involves only $2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}$. We deduce from this that $O(\mathsf{U}, \mathsf{V}, \mathsf{W})$ must certainly include the term

$$(70)\qquad \frac{1}{T}\left(\mathsf{U}\frac{\partial T}{\partial x}+\mathsf{V}\frac{\partial T}{\partial y}+\mathsf{W}\frac{\partial T}{\partial z}\right)P_1(C^2),$$

and that $E(U, V, W)$ must similarly include the term

$$(71) \qquad (c_{11}U^2+c_{22}V^2+c_{33}W^2+c_{23}VW+c_{31}WV+c_{12}UV)\,P(C^2),$$

where

$$(72) \qquad \left\{ \begin{aligned} c_{11} &= 2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{dz}, & c_{23} &= 3\left(\frac{\partial v_0}{\partial z}+\frac{\partial w_0}{\partial y}\right), \\ c_{22} &= 2\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{dz}-\frac{\partial u_0}{\partial x}, & c_{31} &= 3\left(\frac{\partial w_0}{\partial x}+\frac{\partial u_0}{\partial z}\right), \\ c_{33} &= 2\frac{\partial w_0}{\partial z}-\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}, & c_{12} &= 3\left(\frac{\partial u_0}{\partial y}+\frac{\partial v_0}{\partial x}\right). \end{aligned} \right.$$

The factor of $P(C^2)$ in (71) is equal to $3S'-C^2S$, by (12) and (15), and is therefore an invariant with respect to an orthogonal transformation of axes.

Further since, by (26) and (30), no other derivatives of T and (u_0, v_0, w_0) occur in $\Delta U_1C_1^{2s}$ or $\Delta U_1^2C_1^{2s}$, we conclude that none such appear in $F(U, V, W)$—at any rate, to our degree of approximation; thus the other terms in (12)–(15), while they possess the invariant property, do not satisfy the other conditions which must be fulfilled by $F(U, V, W)$.

We therefore conclude that $F(U, V, W)$ is composed only of (70) and (71) to our order of accuracy, and we shall suppose that the two functions $P(C^2)$ are expansible as power series in C^2. Throughout this paper we shall assume that all convergency conditions necessary for the validity of our analysis are satisfied; the justification of this assumption would offer serious difficulty, and the investigation would lead us into regions of pure mathematics which are largely unexplored, and would be unsuitable in the present paper. In § 10 we shall see that numerical approximations for the most important molecular models confirm the assumption of convergence sufficiently for our purpose.

It is convenient to write our expression for $F(U, V, W)$ in the form

$$(73) \quad F(U, V, W) = -B_0\frac{1}{T}\left(U\frac{\partial T}{\partial x}+V\frac{\partial T}{\partial y}+W\frac{\partial T}{\partial z}\right)\sum_{r=0}^{\infty}\frac{(2hm)^r}{1\,.\,3\,.\,5\,\ldots\,(2r+3)\,r}\,\beta_{r-1}C^{2r}$$

$$-C_0 2hm\,(c_{11}U^2+c_{22}V^2+c_{33}W^2+c_{23}VW+c_{31}WU+c_{12}UV)\sum_{r=0}^{\infty}\frac{(2hm)^r}{1\,.\,3\,.\,5\,\ldots\,(2r+5)}\,\gamma_r C^{2r}.$$

In the first line, when $r = 0$, the factor r in the denominator is to be omitted. The suffix 1 or 2 must be added to m, U, V, W, C, β, γ when we wish to distinguish between $F_1(U_1, V_1, W_1)$ and $F_2(U_2, V_2, W_2)$.

Since, by (72),

$$(74) \qquad c_{11}+c_{22}+c_{33} = 0,$$

it is easy to see that (18) is satisfied by this form of F, while in order to satisfy (17) we must have

$$\beta_{-1}+\sum_{0}^{\infty}\beta_r/(r+1) = 0. \tag{75}$$

The products $B_0\beta_r$, $B_0\gamma_r$ are quite definite, but B_0 and C_0 can evidently be assigned arbitrarily; we shall decide that their values, though unspecified for the present, are alike for F_1 and F_2.

The above expression for $F(\mathsf{U}, \mathsf{V}, \mathsf{W})$ is equivalent to that obtained by ENSKOG (§ 1), by an entirely different method. But the chief difficulty of our problem, and one hitherto unsolved, lies in the determination of the coefficients β and γ; this is effected in the present paper by means of ΔQ.

§ 7. THE CALCULATION OF ΔQ_1.

§ 7 (A) In calculating ΔQ_1 we shall deal chiefly with $\Delta_{12}Q_1$ (*cf.* § 5 (A) and (67)). The particular forms of Q_1 which we shall consider are

$$Q_1 = (2hm_1)^{s+\frac{1}{2}}\mathsf{U}_1 C_1^{2s} \equiv \mathfrak{B}_1^{(s)}, \tag{76}$$

$$Q_1 = (2hm_1)^{s+1}\mathsf{U}_1^2 C_1^{2s} \equiv \mathfrak{C}_1^{(s)}. \tag{77}$$

In accordance with § 5 (D), the only part of $F(\mathsf{U}, \mathsf{V}, \mathsf{W})$ which is relevant to $\Delta\mathfrak{B}_1^{(s)}$ is

$$-B_0\frac{1}{T}\frac{\partial T}{\partial x}\mathsf{U}\sum_{0}^{\infty}\frac{(2hm)^r}{1\,.\,3\,.\,5\,\ldots\,(2r+3)\,r}\beta_{r-1}C^{2r}, \tag{78}$$

while that which alone concerns $\Delta\mathfrak{C}_1^{(s)}$ is

$$-2hmC_0\left(c_{11}\mathsf{U}^2+c_{22}\mathsf{V}^2+c_{33}\mathsf{W}^2\right)\sum_{0}^{\infty}\frac{(2hm)^r}{1\,.\,3\,.\,5\,\ldots\,(2r+5)}\gamma_r C^{2r}. \tag{79}$$

As to the latter, since the remainder of the integrand of $\Delta\mathfrak{C}_1^{(s)}$ is symmetrical with respect to V and W, the parts of this integral arising from V^2 and W^2 in (79) are equal, so that $c_{22}\mathsf{V}^2+c_{33}\mathsf{W}^2$ can be replaced by $\frac{1}{2}(c_{22}+c_{33})(\mathsf{V}^2+\mathsf{W}^2) = -\frac{1}{2}c_{11}(C^2-\mathsf{U}^2)$, by (74). Hence for our purpose (79) is equivalent to

$$-\tfrac{1}{2}(2hm)\,C_0c_{11}\left(3\mathsf{U}^2-C^2\right)\sum_{0}^{\infty}\frac{(2hm)^r}{1\,.\,3\,.\,5\,\ldots\,(2r+5)}\gamma_r C^{2r}. \tag{80}$$

We shall denote by $b_{12}(r_1s_1)$ the part of $\Delta_{12}\mathfrak{B}_1^{(s)}$ which arises from the term $-(2hm_1)^{r+\frac{1}{2}}\mathsf{U}_1C_1^{2r}$ in $F_1(\mathsf{U}_1, \mathsf{V}_1, \mathsf{W}_1)$, and by $b_{12}(r_2s_1)$ the part arising from the corresponding term of $F_2(\mathsf{U}_2, \mathsf{V}_2, \mathsf{W}_2)$, in each case the numerical and other factors in F being excluded.[*] The corresponding portions of $\mathrm{I}_1(\chi_{12})$ will be denoted by $\mathrm{I}(r_1s_1, \chi_{12})$ and $\mathrm{I}(r_2s_1, \chi_{12})$ respectively. Then

$$(81)\qquad \mathrm{I}(r_1s_1, \chi_{12}) = \int\!\!\int\!\!\int\!\!\int\!\!\int (2h\mu_1m_0)^{r+s+1}\,\mathrm{U}'_1\mathrm{C}'^{2s}_1\mathrm{U}_1\mathrm{C}_1^{2r}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_{\mathrm{R}}\,d\phi_0\,d\phi_{\mathrm{R}},$$

$$(82)\qquad \mathrm{I}(r_2s_1, \chi_{12}) = \int\!\!\int\!\!\int\!\!\int\!\!\int (2hm_0)^{r+s+1}\mu_1^{s+\frac{1}{2}}\mu_2^{r+\frac{1}{2}}\,\mathrm{U}'_1\mathrm{C}'^{2s}_1\mathrm{U}_2\mathrm{C}_2^{2r}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_{\mathrm{R}}\,d\phi_0\,d\phi_{\mathrm{R}},$$

$$(83)\qquad b_{12}(r_1s_1) = -\nu_1\nu_2(\mu_1\mu_2)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3$$
$$\int\!\!\int\!\!\int e^{-hm_0(\mathrm{C}_0^2+\mathrm{C}_{\mathrm{R}}^2)}\{\mathrm{I}(r_1s_1, \chi_{12})-\mathrm{I}(r_1s_1, 0)\}\,\mathrm{C}_0^2\mathrm{C}_{\mathrm{R}}^3\,p\,dp\,d\mathrm{C}_0\,d\mathrm{C}_{\mathrm{R}},$$

$$(84)\qquad b_{12}(r_2s_1) = -\nu_1\nu_2(\mu_1\mu_2)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3$$
$$\int\!\!\int\!\!\int e^{-hm_0(\mathrm{C}_0^2+\mathrm{C}_{\mathrm{R}}^2)}\{\mathrm{I}(r_2s_1, \chi_{12})-\mathrm{I}(r_2s_1, 0)\}\,\mathrm{C}_0^2\mathrm{C}_{\mathrm{R}}^3\,p\,dp\,d\mathrm{C}_0\,d\mathrm{C}_{\mathrm{R}}.$$

The similar quantities relating to $\Delta_{12}\mathfrak{C}_1^{(s)}$ will be denoted by $c_{12}(r_1s_1)$, $c_{12}(r_2s_1)$ and $\mathrm{J}(r_1s_1, \chi_{12})$, $\mathrm{J}(r_2s_1, \chi_{12})$ respectively, so that

$$(85)\qquad \mathrm{J}(r_1s_1, \chi_{12})$$
$$= \int\!\!\int\!\!\int\!\!\int\!\!\int \tfrac{1}{2}(2h\mu_1m_0)^{r+s+2}\,\mathrm{U}'^2_1\mathrm{C}'^{2s}_1(3\mathrm{U}_1^2-\mathrm{C}_1^2)\,\mathrm{C}_1^{2r}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_{\mathrm{R}}\,d\phi_0\,d\phi_{\mathrm{R}},$$

$$(86)\qquad \mathrm{J}(r_2s_1, \chi_{12})$$
$$= \int\!\!\int\!\!\int\!\!\int\!\!\int \tfrac{1}{2}(2hm_0)^{r+s+2}\mu_1^{s+1}\mu_2^{r+1}\,\mathrm{U}'^2_1\mathrm{C}'^{2s}_1(3\mathrm{U}_2^2-\mathrm{C}_2^2)\,\mathrm{C}_2^{2r}\,d\epsilon\,d\cos\theta_0\,d\cos\theta_{\mathrm{R}}\,d\phi_0\,d\phi_{\mathrm{R}},$$

$$(87)\qquad c_{12}(r_1s_1) = -\nu_1\nu_2(\mu_1\mu_2)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3$$
$$\int\!\!\int\!\!\int e^{-hm_0(\mathrm{C}_0^2+\mathrm{C}_{\mathrm{R}}^2)}\{\mathrm{J}(r_1s_1, \chi_{12})-\mathrm{J}(r_1s_1, 0)\}\,\mathrm{C}_0^2\mathrm{C}_{\mathrm{R}}^3\,p\,dp\,d\mathrm{C}_0\,d\mathrm{C}_{\mathrm{R}},$$

$$(88)\qquad c_{12}(r_2s_1) = -\nu_1\nu_2(\mu_1\mu_2)^{-1/2}\left(\frac{hm_0}{\pi}\right)^3$$
$$\int\!\!\int\!\!\int e^{-hm_0(\mathrm{C}_0^2+\mathrm{C}_{\mathrm{R}}^2)}\{\mathrm{J}(r_2s_1, \chi_{12})-\mathrm{J}(r_2s_1, 0)\}\,\mathrm{C}_0^2\mathrm{C}_{\mathrm{R}}^3\,p\,dp\,d\mathrm{C}_0\,d\mathrm{C}_{\mathrm{R}}.$$

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[*] We have here *included* a factor $(2hm)^{1/2}$ which does not occur in F; this will be allowed for subsequently.

The Integration with respect to θ_R, ϕ_R, ϕ_0.

§ 7 (B) In $I(rs, \chi_{12})$ and $J(rs, \chi_{12})$ it is clear from (48) to (53) that ϕ_R does not appear at all in the integrand, while θ_R and ϕ_0 occur only in the products U'_1U and $U'^2_1(3U^2-C^2)$ respectively. We have

$$U'_1U_1 = C_0^2\cos^2\lambda+\mu_{21}C_R^2\cos\theta_R\cos\theta'_R+\mu_{21}{}^{1/2}C_0C_R\cos\lambda\,(\cos\theta_R+\cos\theta'_R),$$

$$U'_1U_2 = C_0^2\cos^2\lambda-C_R^2\cos\theta_R\cos\theta'_R+C_0C_R\cos\lambda\,(\mu_{21}{}^{1/2}\cos\theta'_R-\mu_{12}{}^{1/2}\cos\theta_R),$$

and, remembering the values of $\cos\lambda$ and $\cos\theta'_R$, we have

$$\iiint U'_1U_1\,d\cos\theta_R\,d\phi_0\,d\phi_R = \tfrac{8}{3}\pi^2\{C_0^2+\mu_{21}C_R^2\cos\chi_{12}-\mu_{21}{}^{1/2}C_0C_R(\cos\theta_0+\cos\theta'_0)\},$$

$$\iiint U'_1U_2\,d\cos\theta_R\,d\phi_0\,d\phi_R = \tfrac{8}{3}\pi^2\{C_0^2-C_R^2\cos\chi_{12}+C_0C_R(\mu_{21}{}^{1/2}\cos\theta'_0-\mu_{12}{}^{1/2}\cos\theta_0)\}.$$

In the notation of (53) the latter two equations may be conveniently re-written as follows :—

$$\mu_1\iiint U'_1U_1\,d\cos\theta_R\,d\phi_0\,d\phi_R = \tfrac{4}{3}\pi^2\{\Theta_{12}(\cos\theta_0)+\Theta_{12}(\cos\theta'_0)-2\mu_2C_R^2(1-\cos\chi_{12})\}.$$

$$\begin{aligned}(\mu_1\mu_2)^{1/2}\iiint U'_1U_2\,d\cos\theta_R\,d\phi_0\,d\phi_R = \tfrac{4}{3}\pi^2\{&\mu_{12}{}^{1/2}\Theta_{21}(\cos\theta_0)+\mu_{21}{}^{1/2}\Theta_{12}(\cos\theta'_0)\\ &+2(\mu_1\mu_2)^{1/2}C_R^2(1-\cos\chi)-(\mu_1\mu_2)^{-1/2}C_R^2\}.\end{aligned}$$

Substituting in (81) and (82), we thus have

$$(89)\quad I(r_1s_1, \chi_{12}) = \tfrac{4}{3}\pi^2(2hm_0)^{r+s+1}\iint\{\Theta_{12}+\Theta'_{12}-2\mu_2C_R^2(1-\cos\chi_{12})\}\,\Theta'^s_{12}\Theta^r_{12}\,d\epsilon\,d\cos\theta_0,$$

$$\begin{aligned}(90)\quad I(r_2s_1, \chi_{12}) = \tfrac{4}{3}\pi^2(2hm_0)^{r+s+1}\iint\{&\mu_{12}{}^{1/2}\Theta_{21}+\mu_{21}{}^{1/2}\Theta'_{12}+2(\mu_1\mu_2)^{1/2}C_R^2(1-\cos\chi_{12})\\ &-(\mu_1\mu_2)^{-1/2}C_R^2\}\,\Theta'^s_{12}\Theta^r_{12}\,d\epsilon\,d\cos\theta_0.\end{aligned}$$

§ 7 (C) In the case of $J(rs, \chi_{12})$, we have

$$(91)\qquad \mu_1^2U'^2_1U_1^2 = (\mu_1{}^{1/2}C_0\cos\lambda+u_2{}^{1/2}C_R\cos\theta_R)^2(\mu_1{}^{1/2}C_0\cos\lambda-\mu_2{}^{1/2}C_R\cos\theta'_R)^2,$$

in which (*cf.* the figure on p. 293) $\lambda = c_0Ox$, $\theta_R = c_ROx$, $\theta'_R = c'_ROx$. In the integration over the sphere, with respect to θ_R and ϕ_0, since θ_0, ϵ, χ_{12} are constant the triangle $c_0c_Rc'_R$ preserves its form, so that we may, if we please, regard x as the variable point and $c_0c_Rc'_R$ as fixed. Now it may readily be proved, by the method of "poles" in the theory of harmonic functions, that if A, B, C are three fixed points on a unit sphere, and P a variable point, then the integral over the spherical surface of

$$\cos^2 PA\cos PB\cos PC$$

is

$$\tfrac{1}{15}\pi\,(2\cos AB\cos AC+\cos BC).$$

Applying this result to (91), identifying A, B, C with one or more of the points c_0, c_R, c'_R, and P with x, we may with but little difficulty prove that

$$\mu_1^2 \iiint U'^2_1 U_1^2 \, d\cos\theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{15}\pi^2 \{\Theta_{12}^2 + 4\Theta_{12}\Theta'_{12} + \Theta'^2_{12} - 4\mu_2 C_R^2 (\Theta_{12}+\Theta'_{12})(1-\cos\chi_{12}) + 4\mu_2^2 C_R^4 (1-\cos\chi_{12})^2\}.$$

Similarly we may show that

$$\mu_1 \iiint U'^2_1 \, d\cos\theta_R \, d\phi_0 \, d\phi_R = \tfrac{8}{3}\pi^2 \Theta'_{12},$$

so that

$$\mu_1^2 \iiint U'^2_1 (3U_1^2 - C_1^2) \, d\cos\theta_R \, d\phi_0 \, d\phi_R = \tfrac{4}{5}\pi^2 \{\Theta_{12}^2 + \tfrac{2}{3}\Theta_{12}\Theta'_{12} + \Theta'^2_{12} - 4\mu_2 C_R^2 (\Theta_{12}+\Theta'_{12})(1-\cos\chi_{12}) + 4\mu_2^2 C_R^4 (1-\cos\chi_{12})^2\}.$$

Hence we have

$$(92) \quad J(r_1 s_1, \chi_{12}) = \tfrac{2}{5}\pi^2 (2hm_0)^{r+s+2} \iint \{\Theta_{12}^2 + \tfrac{2}{3}\Theta_{12}\Theta'_{12} + \Theta'^2_{12} - 4\mu_2 C_R^2 (\Theta_{12}+\Theta'_{12})(1-\cos\chi_{12}) + 4\mu_2^2 C_R^4 (1-\cos\chi_{12})^2\} \Theta'^s_{12} \Theta^r_{12} \, d\epsilon \, d\cos\theta_0,$$

and it may be proved in a similar manner that

$$(93) \quad J(r_2 s_1, \chi_{12}) = \tfrac{2}{5}\pi^2 (2hm_0)^{r+s+2} \iint [\mu_{12}\Theta_{21}^2 + \tfrac{2}{3}\Theta_{21}\Theta'_{12} + \mu_{21}\Theta'^2_{12} + 2C_R^2 (\mu_{12}^{1/2}\Theta_{21} + \mu_{21}^{1/2}\Theta'_{12}) \{2(\mu_1\mu_2)^{1/2}(1-\cos\chi_{12}) - (\mu_1\mu_2)^{-1/2}\} + C_R^4 \{2(\mu_1\mu_2)^{1/2}(1-\cos\chi_{12}) - (\mu_1\mu_2)^{-1/2}\}^2] \Theta'^s_{12} \Theta^r_{21} \, d\epsilon \, d\cos\theta_0.$$

The Expansion of $(\rho^2+\sigma^2-2\rho\sigma\cos\theta)^n$ *in a* LEGENDRE'S *Series.*

§ 7 (D) In order to effect the integration of I and J with respect to ϵ and θ_0 we must have recourse to the expansion of

$$(94) \qquad P_n(\rho, \sigma, \cos\theta) \equiv (\rho^2+\sigma^2-2\rho\sigma\cos\theta)^n$$

in a series of LEGENDRE'S functions. In a recent paper* I have shown that

$$(95) \qquad P_n(\rho, \sigma, \cos\theta) = \sum_{k=0}^{n} (-1)^k (2k+1)\, {}^nA^k(\rho^2, \sigma^2)\, P_k(\cos\theta),$$

where $P_k(\cos\theta)$ is the ordinary LEGENDRE'S function of $\cos\theta$, of type k, and†

$$(96) \qquad {}^nA^k(\rho^2, \sigma^2) = \left(\frac{\rho}{\sigma}\right)^k \sum_{t=k}^{n} \frac{n_t}{(t+\frac{1}{2})_t} \frac{(n+\frac{1}{2})_{t-k}}{(t-k)_{t-k}} \rho^{2(r-t)} \sigma^{2t}$$

$$= \left(\frac{\sigma}{\rho}\right)^k \sum_{t=k}^{n} \frac{n_t}{(t+\frac{1}{2})_t} \frac{(n+\frac{1}{2})_{t-k}}{(t-k)_{t-k}} \sigma^{2(r-t)} \rho^{2t}.$$

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* CHAPMAN, 'Quarterly Journal of Mathematics,' p. 16, 1916. The expansion is there not limited to integral values of n, though these are alone considered in the present paper.

† The constant k is necessarily a positive integer; if $k > n$, ${}^nA^k = 0$.

In the last equation the symbol p_q, where q is integral, is defined thus :—

(97) $$p_q = p(p-1)(p-2)\dots(p-q+1).$$

From (53) it is clear that

(98) $$\{\Theta_{12}(\cos\theta)\}^n = \mathrm{P}_n(\mu_1\mathrm{C}_0^2, \mu_2\mathrm{C}_\mathrm{R}^2, -\cos\theta) = \sum_{k=0}^{n}(2k+1)\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\theta),$$

(99) $$\{\Theta_{21}(\cos\theta)\}^n = \mathrm{P}_n(\mu_2\mathrm{C}_0^2, \mu_1\mathrm{C}_\mathrm{R}^2, \cos\theta) = \sum_{k=0}^{n}(-1)^k(2k+1)\,{}^n\mathrm{A}^k_{21}\,\mathrm{P}_k(\cos\theta),$$

where we have written, for brevity,

(100) $${}^n\mathrm{A}^k_{12} \equiv {}^n\mathrm{A}^k(\mu_1\mathrm{C}_0^2, \mu_2\mathrm{C}_\mathrm{R}^2) \qquad {}^n\mathrm{A}^k_{21} = {}^n\mathrm{A}^k(\mu_2\mathrm{C}_0^2, \mu_1\mathrm{C}_\mathrm{R}^2).$$

In our expressions for $\Delta\mathrm{Q}_1$, θ takes the values θ_0 and θ'_0, and the variable ϵ is involved only through the latter angle, which occurs in Θ'_{12} or $\Theta_{12}(\cos\theta'_0)$. In the expansion of the latter (*cf.* 98) in terms of $\mathrm{P}_k(\cos\theta'_0)$, or, by (48), of $\mathrm{P}_k(\cos\theta_0\cos\chi_{12}+\sin\theta_0\sin\chi_{12}\cos\epsilon)$, we shall make use of the following well-known formula in the theory of spherical harmonic functions :—

(101) $$\begin{aligned}\mathrm{P}_k(\cos\theta'_0) &= \mathrm{P}_k(\cos\theta_0\cos\chi_{12}+\sin\theta_0\sin\chi_{12}\cos\epsilon)\\ &= \mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12})+2\sum_{l=1}^{k}\frac{(k-l)\,!}{(k+l)\,!}\,\mathrm{P}_k^l(\cos\theta)\,\mathrm{P}_k^l(\cos\chi_{12})\cos l\epsilon.\end{aligned}$$

The Integration with respect to ϵ and θ_0.

§ 7 (E) Since the integral of $\cos l\epsilon$ with respect to ϵ, between 0 and 2π, is zero unless $l=0$, from (98) and (101) we deduce the result,

(102) $$\int_0^{2\pi}\Theta'^{\,n}_{12}\,d\epsilon = 2\pi\sum_{k=0}^{n}(2k+1)\,{}^n\mathrm{A}^k_{12}\mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12}).$$

Now from (89), (90), and (92), (93), it is evident that as far as concerns integration with respect to ϵ and θ_0 we have to consider a number of terms such as

(103) $$\iint\Theta^m\Theta'^{\,n}_{12}\,d\epsilon\,d\cos\theta_0,$$

where Θ^m may have the suffix 12 or 21, while Θ'^n always has the suffix 12. Now Θ^m does not involve ϵ, so that (102) suffices for the integration with respect to ϵ, and leaves us with

(104) $$2\pi\int_{-1}^{1}\left\{\sum_{k=0}^{m}(\pm1)^k(2k+1)\,{}^m\mathrm{A}^k\mathrm{P}_k(\cos\theta_0)\right\}\left\{\sum_{k=0}^{n}(2k+1)\,{}^n\mathrm{A}^k_{12}\mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_k(\cos\chi_{12})\right\}d\cos\theta_0$$

in place of (103); in the first bracket the ambiguous sign is to be + in the case of $\Theta_{12}{}^m$, and − in that of $\Theta_{21}{}^m$.

By the theory of LEGENDRE's functions we have

$$(2k+1)\int_{-1}^{1} \mathrm{P}_k(\cos\theta_0)\,\mathrm{P}_l(\cos\theta_0)\,d\cos\theta_0 = 0 \qquad \text{if } k \neq l.$$

$$(2k+1)\int_{-1}^{1} \{\mathrm{P}_k(\cos\theta_0)\}^2\,d\cos\theta_0 = 2.$$

Consequently

$$(105) \qquad \iint \Theta_{12}{}^m\Theta'_{12}{}^n\,d\epsilon\,d\cos\theta_0 = 4\pi\sum_{k=0}^{m,\,n}(2k+1)\,{}^m\mathrm{A}^k_{12}\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\chi_{12}),$$

$$(106) \qquad \iint \Theta_{21}{}^m\Theta'_{12}{}^n\,d\epsilon\,d\cos\theta_0 = 4\pi\sum_{k=0}^{m,\,n}(-1)^k(2k+1)\,{}^m\mathrm{A}^k_{21}\,{}^n\mathrm{A}^k_{12}\,\mathrm{P}_k(\cos\chi_{12}),$$

where the upper limit of k is the lesser of the two integers m, n.

Applying these results to (89), (90), (92), (93), we have, therefore,

$$\begin{aligned}(107) \quad \mathrm{I}(r_1s_1,\chi_{12}) = \tfrac{16}{3}\pi^3(2hm_0)^{r+s+1} & \\ \sum_{k=0}^{r+1,\,s+1}\Big\{ & {}^{r+1}\mathrm{A}^k_{12}\,{}^s\mathrm{A}^k_{12} + {}^r\mathrm{A}^k_{12}\,{}^{s+1}\mathrm{A}^k_{12} \\ & -2\mu_2\mathrm{C}^2_{\mathrm{R}}\,{}^r\mathrm{A}^k_{12}\,{}^s\mathrm{A}^k_{12}(1-\cos\chi_{12})\Big\}\,\mathrm{P}_k(\cos\chi_{12}),\end{aligned}$$

$$\begin{aligned}(108) \quad \mathrm{I}(r_2s_1,\chi_{12}) = \tfrac{16}{3}\pi^3(2hm_0)^{r+s+1} & \\ \sum_{k=0}^{r+1,\,s+1}(-1)^k\Big[& \mu^{1/2}_{12}\,{}^{r+1}\mathrm{A}^k_{21}\,{}^s\mathrm{A}^k_{12} + \mu^{1/2}_{21}\,{}^r\mathrm{A}^k_{21}\,{}^{s+1}\mathrm{A}^k_{12} \\ & +2\mathrm{C}^2_{\mathrm{R}}\,{}^r\mathrm{A}^k_{21}\,{}^s\mathrm{A}^k_{12}\{(\mu_1\mu_2)^{1/2}(1-\cos\chi_{12}) \\ & -\tfrac{1}{2}(\mu_1\mu_2)^{-1/2}\}\Big]\,\mathrm{P}_k(\cos\chi_{12}),\end{aligned}$$

$$\begin{aligned}(109) \quad \mathrm{J}(r_1s_1,\chi_{12}) = \tfrac{8}{5}\pi^3(2hm_0)^{r+s+2} & \\ \sum_{k=0}^{r+2,\,s+2}\Big[& {}^{r+2}\mathrm{A}^k_{12}\,{}^s\mathrm{A}^k_{12} + \tfrac{2}{3}\,{}^{r+1}\mathrm{A}^k_{12}\,{}^{s+1}\mathrm{A}^k_{12} + {}^r\mathrm{A}^k_{12}\,{}^{s+2}\mathrm{A}^k_{12} \\ & -4\mu_2\mathrm{C}^2_{\mathrm{R}}({}^{r+1}\mathrm{A}^k_{12}\,{}^s\mathrm{A}^k_{12} + {}^r\mathrm{A}^k_{12}\,{}^{s+1}\mathrm{A}^k_{12})(1-\cos\chi_{12}) \\ & +4\mu^2_2\mathrm{C}^4_{\mathrm{R}}\,{}^r\mathrm{A}^k_{12}\,{}^s\mathrm{A}^k_{12}(1-\cos\chi_{12})^2\Big]\,\mathrm{P}_k(\cos\chi_{12}),\end{aligned}$$

$$\begin{aligned}(110) \quad \mathrm{J}(r_2s_1,\chi_{12}) = \tfrac{8}{5}\pi^3(2hm_0)^{r+s+2} & \\ \sum_{k=0}^{r+2,\,s+2}(-1)^k\Big[& \mu_{12}\,{}^{r+2}\mathrm{A}^k_{21}\,{}^s\mathrm{A}^k_{12} + \tfrac{2}{3}\,{}^{r+1}\mathrm{A}^k_{21}\,{}^{s+1}\mathrm{A}^k_{12} + \mu_{21}\,{}^r\mathrm{A}^k_{21}\,{}^{s+2}\mathrm{A}^k_{12} \\ & +2\mathrm{C}^2_{\mathrm{R}}(\mu_{12}{}^{1/2}\,{}^{r+1}\mathrm{A}^k_{21}\,{}^s\mathrm{A}^k_{12} + \mu_{21}{}^{1/2}\,{}^r\mathrm{A}^k_{21}\,{}^{s+1}\mathrm{A}^k_{12})\{2(\mu_1\mu_2)^{1/2}(1-\cos\chi_{12})-(\mu_1\mu_2)^{-}\} \\ & +\mathrm{C}^4_{\mathrm{R}}\,{}^r\mathrm{A}^k_{21}\,{}^s\mathrm{A}^k_{12}\{2(\mu_1\mu_2)^{1/2}(1-\cos\chi_{12})-(\mu_1\mu_2)^{-1/2}\}^2\Big]\,\mathrm{P}_k(\cos\chi_{12}).\end{aligned}$$

The Integration with respect to p.

§ 7 (F) On referring back to equations (81) to (88) it is clear that before executing the integration with respect to p, in the calculation of $b(rs)$ and $c(rs)$, we must subtract from $I(rs, \chi_{12})$ and $J(rs, \chi_{12})$, as given by (107) to (110), their values corresponding to $\chi_{12} = 0$. Now when $\chi_{12} = 0$, we have

$$1-\cos\chi_{12} = 0, \qquad P_k(\cos\chi_{12}) = 1.$$

Thus where $P_k(\cos\chi_{12})$ occurs alone in (107) to (110), it must be replaced by $P_k(\cos\chi_{12})-1$ in the expressions for $b(rs)$ and $c(rs)$, the terms $P_k(\cos\chi_{12})(1-\cos\chi_{12})$ and $P_k(\cos\chi_{12})(1-\cos\chi_{12})^2$ remaining unchanged, since the corresponding terms in $I(rs, 0)$ and $J(rs, 0)$ vanish.

The variable p is involved in $b(rs)$ and $c(rs)$ only through $p\,dp$ and χ_{12}, the latter being also a function of C_R. We may therefore formally execute the integration with respect to p by writing

$$(111) \qquad \phi^k_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty \{1-P_k(\cos\chi_{12})\}\, p\,dp,$$

$$(112) \qquad \phi'^k_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty (1-\cos\chi_{12})\, P_k(\cos\chi_{12})\, p\,dp,$$

$$(113) \qquad \phi''^k_{12}(C_R) \equiv (2k+1)(\mu_1\mu_2)^{-1/2} C_R \int_0^\infty (1-\cos\chi_{12})^2\, P_k(\cos\chi_{12})\, p\,dp.$$

The nature of these functions depends on the law of inter-action between molecules at collisions, and by keeping this law unspecified we retain the utmost generality in our theory, which implies no property of the molecules save that of spherical symmetry.

By means of the well-known equation

$$(114) \qquad (k+1)P_{k+1}(\cos\chi)-(2k+1)\cos\chi P_k(\cos\chi)+kP_{k-1}(\cos\chi) = 0$$

the function $\phi'^k_{12}(C_R)$ can be expressed in terms of $\phi^k_{12}(C_R)$, for different values of k, as follows :—

$$(115) \qquad \phi'^k_{12}(C_R) = \frac{k+1}{2k+3}\phi^{k+1}_{12}(C_R) - \phi^k_{12}(C_R) + \frac{k}{2k-1}\phi^{k-1}_{12}(C_R),$$

and by a repeated application of (114) we may obtain a similar expression (involving $\phi^l_{12}(C_R)$ for $l = k, k\pm1, k\pm2$) for $\phi''^k_{12}(C_R)$.

To avoid unnecessary formulæ, we shall not write down the forms taken by $b(rs)$ and $c(rs)$ on substitution of the results of this section till after we have considered the next step in the integration.

The Integration with respect to C_0 *and* C_R.

§ 7 (G) In the expressions for $b\,(rs)$ and $c\,(rs)$, integrated out with respect to all the variables save C_0 and C_R, it is now convenient to make the transformation

$$(116) \qquad x^2 = hm_0 C_0^{\,2}, \qquad y^2 = hm_0 C_R^{\,2}.$$

In connection with this we shall use the following notation :—

$$(117)\quad B^k_{1212}(m,\,n) \equiv (2hm_0)^{m+n}\,{}^m A^k_{12}\,{}^n A^k_{12} = (2hm_0)^{m+n}\,.\,{}^m A^k(\mu_1 C_0^{\,2},\,\mu_2 C_R^{\,2})\,.\,{}^n A^k(\mu_1 C_0^{\,2},\,\mu_2 C_R^{\,2})$$

$$= {}^m A^k(2\mu_1 hm_0 C_0^{\,2},\,2\mu_2 hm_0 C_R^{\,2})\,.\,{}^n A^k(2\mu_1 hm_0 C_0^{\,2},\,2\mu_2 hm_0 C_R^{\,2}),$$

$$= {}^m A^k(2\mu_1 x^2,\,2\mu_2 y^2)\,.\,{}^n A^k(2\mu_1 x^2,\,2\mu_2 y^2),$$

$$(118)\quad B^k_{2112}(m,\,n) = (2hm_0)^{m+n}\,.\,{}^m A^k_{21}\,{}^n A^k_{12},$$

$$= {}^m A^k(2\mu_2 x^2,\,2\mu_1 y^2)\,.\,{}^n A^k(2\mu_1 x^2,\,2\mu_2 y^2).$$

We have here used the fact—*cf.* (96)–(100)—that ${}^n A^k(\rho^2,\,\sigma^2)$ is a homogeneous polynomial of degree $2n$ in ρ, σ.

We now use equations (83), (84), (107), (108), in conjunction with § 7 (F), to write down the following expressions* for $b\,(r,\,s)$, taking particular note of the signs of the various terms :—

$$(119)\quad b_{12}(r_1 s_1) = \tfrac{16}{3}\nu_1\nu_2 \iint e^{-(x^2+y^2)} \sum_{k=0}^{r+1,\,s+1} \big[\phi^k_{12}(\tau_{12}y)\{B^k(r+1,\,s)+B^k(r,\,s+1)\}$$

$$+\,4\mu_2 y^2 \phi'^k_{12}(\tau_{12}y)\,B^k(r,\,s)\big]_{1212}\,x^2y^2\,dx\,dy,$$

$$(120)\quad b_{12}(r_2 s_1) = \tfrac{16}{3}\nu_1\nu_2 \iint e^{-(x^2+y^2)} \sum_{k=0}^{r+1,\,s+1} (-1)^k\big[\phi^k_{12}(\tau_{12}y)\{\mu_{12}^{\,1/2}B^k(r+1,s)$$

$$-\,2\,(\mu_1\mu_2)^{-1/2}y^2 B^k(r,\,s)+\mu_{21}^{\,1/2}B^k(r,\,s+1)\}$$

$$-\,4\,(\mu_1\mu_2)^{1/2}y^2\phi'^k_{12}(\tau_{12}y)\,B^k(r,s)\big]_{2112}\,x^2y^2\,dx\,dy.$$

In a similar way, from (87), 88), (109), (110) we obtain the following expressions for $c\,(r,\,s)$:—

$$(121)\quad c_{12}(r_1 s_1) = \tfrac{8}{5}\nu_1\nu_2 \iint e^{-(x^2+y^2)} \sum_{k=0}^{r+2,\,s+2} \big[\phi^k_{12}(\tau_{12}y)\{B^k(r+2,\,s)+\tfrac{2}{3}B^k(r+1,\,s+1)$$

$$+\,B^k(r,\,s+2)\}+8\mu_2 y^2\phi'^k_{12}(\tau_{12}y)\{B^k(r+1,\,s)$$

$$+\,B^k(r,\,s+1)\}-16\mu_2^{\,2}y^4\phi''^k_{12}(\tau_{12}y)\,B^k(r,\,s)\big]_{1212}\,x^2y^2\,dx\,dy.$$

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* In (119)–(122) the suffixes 1212 or 2112, which should be appended to the symbols $B^k(m,\,n)$—the same for all those within any one square bracket—are for convenience of printing indicated only by being placed after the bracket itself.

$$
\begin{aligned}
(122)\quad c_{12}(r_2 s_1) = \tfrac{8}{5}\nu_1\nu_2 \iint e^{-(x^2+y^2)} \sum_{k=0}^{r+2,\, s+2} (-1)^k \big[& \phi^k{}_{12}(\tau_{12}y)\{\mu_{12}\mathrm{B}^k(r+2,\ s)+\tfrac{2}{3}\mathrm{B}^k(r+1,\ s+1) \\
& +\mu_{21}\mathrm{B}^k(r,\ s+2)-4(\mu_1\mu_2)^{-1/2}y^2\Big(\mu_{12}{}^{1/2}\mathrm{B}^k(r+1,\ s) \\
& +\mu_{21}{}^{1/2}\mathrm{B}^k(r,\ s+1)\Big)+4\mu_1\mu_2 y^4\mathrm{B}^k(r,\ s)\} \\
& -8\,(\mu_1\mu_2)^{1/2}y^2\phi'^k{}_{12}(\tau_{12}y)\{\mu_{12}{}^{1/2}\mathrm{B}^k(r+1,\ s) \\
& -2\,(\mu_1\mu_2)^{-1/2}y^2\mathrm{B}^k(r,\ s)+\mu_{21}{}^{1/2}\mathrm{B}^k(r,\ s+1)\} \\
& -16\mu_1\mu_2 y^4\phi''^k{}_{12}(\tau_{12}y)\,\mathrm{B}^k(r,\ s)\big]_{2112}\, x^2y^2\,dx\,dy.
\end{aligned}
$$

The symbol τ in $\phi^k{}_{12}(\tau_{12}y)$ is defined by the equation

$$(123)\qquad \tau_{12} = \frac{1}{\sqrt{hm_0}}.$$

The integration with respect to x in the above expressions is of a quite elementary nature, but it will not be executed in general terms owing to the complexity of the polynomials $\mathrm{B}^k(r,\ s)$, which are integral in x^2. Any individual term in the integrands of (119) to (122) is of the form (so far as concerns x)

$$(124)\qquad \int_0^\infty e^{-x^2}x^{2(m+1)}\,dx = \tfrac{1}{4}\pi^{1/2}(m+\tfrac{1}{2})_m.$$

The integration with respect to y will similarly not be executed in general; in any case, owing to the unspecified functions $\phi^k{}_{12}(\tau y)$, this integration could be only formally completed, and until we come to consider special types of molecular models we shall be content to leave $b(r,\ s)$ and $c(r,\ s)$ in the above form.

The Complete Expression for $\Delta_{12}\mathrm{Q}_1$.

§ 7 (H) On referring back to § 7 (A), and the definition of $b(r,\ s)$, $c(r,\ s)$, it is clear that we are now able to write down the complete expressions for $\Delta_{12}\mathrm{Q}_1$ in the two cases we have considered. This involves taking into account *all* the terms ($r = 0$ to ∞) in $\mathrm{F}(\mathsf{U},\ \mathsf{V},\ \mathsf{W})$, with their appropriate coefficients, as in (78), (80); and in order to make the expressions more symmetrical, it is convenient to change the values of Q_1 slightly, by multiplying them by certain numerical factors (*cf.* 26, 30). Thus writing

$$(125)\qquad \lambda_{r-1,\, s-1} \equiv \frac{1}{1\,.\,3\,.\,5\,\ldots\,(2r+3)\,r\,.\,1\,.\,3\,.\,5\,\ldots\,(2s+3)\,s},$$

$$(126)\qquad \lambda'_{rs} \equiv \frac{1}{1\,.\,3\,.\,5\,\ldots\,(2r+5)\,.\,1\,.\,3\,.\,5\,\ldots\,(2s+5)},$$

we have the following equations for $\Delta_{12}Q_1$ in the two cases under consideration :—

$$(127)\quad \frac{(2hm_1)^{s+1}}{1\,.\,3\,.\,5\ldots(2s+3)\,s}\,\Delta_{12}\mathsf{U}_1\mathrm{C}_1^{\;2s} = \mathrm{B}_0\frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x}\sum_{r=0}^{\infty}\lambda_{r-1,\,s-1}\{\beta_{r-1,\,1}\,b_{12}(r_1s_1)+\mu_{12}{}^{1/2}\beta_{r-1,\,2}\,b_{12}(r_2s_1)\},$$

$$(128)\quad \frac{(2hm_1)^{s+1}}{1\,.\,3\,.\,5\ldots(2s+5)}\,\Delta_{12}\mathsf{U}^2{}_1\mathrm{C}_1^{\;2s} = \mathrm{C}_0c_{11}\sum_{r=0}^{\infty}\lambda'_{rs}\{\gamma_{r,\,1}\,c_{12}\,(r_1s_1)+\gamma_{r,\,2}\,c_{12}\,(r_2s_1)\}.$$

The corresponding values of $\Delta_{11}Q_1$ in the two cases are obtainable from (127), (128) by replacing the suffix 2 by 1 throughout. We will write $b_{11}\,(r_1s_1)$ and $c_{11}\,(r_1s_1)$ respectively for the values taken by $b_{12}\,(r_1s_1)+b_{12}\,(r_2s_1)$ and $c_{12}\,(r_1s_1)+c_{12}\,(r_2s_1)$ when the distinction between the suffixes 2 and 1 in these expressions is abolished. In place of μ_1 and μ_2 we now write $\frac{1}{2}$, and $\mu_{12}=\mu_{21}=1$, $m_0=2m_1$, while $\mathrm{B}^k{}_{12}\,(m,\,n)$ and $\mathrm{B}^k{}_{21}\,(m,\,n)$ become identical, and equal to

$$(129)\qquad {}^m\mathrm{A}^k\,(x^2,\,y^2)\;{}^n\mathrm{A}^k\,(x^2,\,y^2)\equiv \mathrm{B}^k\,(m,\,n).$$

It is convenient to express $b_{11}\,(r_1s_1)$ and $c_{11}\,(r_1s_1)$ in terms of $\phi^k{}_{11}\,(\tau y)$ only, eliminating $\phi''^k{}_{11}\,(\tau y)$ and $\phi'''^k{}_{11}\,(\tau y)$ by means of (115) and a similar equation for $\phi'''^k{}_{11}\,(\tau y)$. When this is done it is found that the coefficient of $\phi^k{}_{11}\,(\tau y)$ vanishes for odd values of k, on account of the factor $(-1)^k$ in $b_{12}\,(r_2s_1)$ and $c_{12}\,(r_2s_1)$. The following are the results thus obtained* :—

$$(130)\quad b_{11}\,(r_1s_1) = \tfrac{32}{3}\nu_1{}^2\iint e^{-(x^2+y^2)}\sum_{k=1}^{(r,\,s)}\phi^{2k}{}_{11}\,(\tau_{11}y)\Big[\mathrm{B}^{2k}\,(r+1,\,s)+\mathrm{B}^{2k}\,(r,\,s+1)$$
$$+2y^2\left\{\frac{2k+1}{4k+1}\mathrm{B}^{2k+1}\,(r,\,s)+\frac{2k}{4k+1}\,\mathrm{B}^{2k-1}\,(r,\,s)-\mathrm{B}^{2k}\,(r,\,s)\right\}\Big]\,x^2y^2\,dx\,dy.$$

$$(131)\quad c_{11}\,(r_1s_1) = \tfrac{16}{5}\nu_1{}^2\iint e^{-(x^2+y^2)}\sum_{k=1}^{[r,\,s]}\phi^{2k}{}_{11}\,(\tau_{11}y)\Big[\mathrm{B}^{2k}(r+2,\,s)+\tfrac{2}{3}\mathrm{B}^{2k}(r+1,\,s+1)+\mathrm{B}^{2k}(r,\,s+2)$$
$$+4y^2\left\{\frac{2k+1}{4k+1}\Big(\mathrm{B}^{2k+1}\,(r+1,\,s)+\mathrm{B}^{2k+1}\,(r,\,s+1)\Big)\right.$$
$$\left.+\frac{2k}{4k+1}\Big(\mathrm{B}^{2k-1}(r+1,\,s)+\mathrm{B}^{2k-1}(r,\,s+1)\Big)-\Big(\mathrm{B}^{2k}(r+1,\,s)+\mathrm{B}^{2k}(r,\,s+1)\Big)\right\}$$
$$+4y^4\left\{\frac{(2k+2)\,(2k+1)}{(4k+3)\,(4k+1)}\,\mathrm{B}^{2k+2}\,(r,\,s)\right.$$
$$+\left(\frac{(2k+1)^2}{(4k+3)\,(4k+1)}+\frac{4k^2}{(4k+1)\,(4k-1)}+1\right)\mathrm{B}^{2k}\,(r,\,s)$$
$$+\frac{2k\,(2k-1)}{(4k+1)\,(4k-1)}\,\mathrm{B}^{2k-2}\,(r,\,s)$$
$$\left.-2\left(\frac{2k+1}{4k+1}\,\mathrm{B}^{2k+1}\,(r,\,s)+\frac{2k}{4k+1}\,\mathrm{B}^{2k-1}\,(r,\,s)\right)\right\}\Big]\,x^2y^2\,dx\,dy.$$

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* In these expressions $\phi^k{}_{11}\,(\tau_{11}y)$ is the equivalent, for an encounter between two molecules of the *same* kind, of $\phi^k{}_{12}\,(\tau_{11}y)$ for molecules of different kinds. Thus (*cf.* 111)

$$\phi^k{}_{11}\,(\tau_{11}y)\equiv 2\,(2k+1)\,\mathrm{C}_{\mathrm{R}}\int_0^{\infty}\{1-\mathrm{P}_k\,(\cos\chi_{11})\}\,p\,dp,$$

where the law connecting χ_{11} with p and C_{R} may differ from that for χ_{12}. Also τ_{11} now becomes $(2hm_1)^{-1/2}$.

The term corresponding to $k = 0$ is absent in both the above cases, since $\phi^0_{11}(\tau_{11}y)$ is itself zero, so that $\phi^2_{11}(\tau_{11}y)$ is the function $\phi_{11}(\tau_{11}y)$ of lowest order ($k = 2$) in $b_{11}(r_1s_1)$ or $c_{11}(r_1s_1)$. The upper limit of k in the case of $b_{11}(r_1s_1)$ is equal to the integral part of the lesser of the two quantities $\frac{1}{2}(r+1)$ and $\frac{1}{2}(s+1)$; this is denoted by (r, s). Similarly the upper limit of k in the case of $c_{11}(r_1s_1)$ is the integral part of the lesser of the two quantities $\frac{1}{2}(r+2)$ and $\frac{1}{2}(s+2)$, which we denote by $[r, s]$. Thus, when $r = 0$ or $s = 0$, $b_{11}(r_1s_1) = 0$.

We can now write down the complete expressions for ΔQ, in the two cases above, as follows:—

$$(132)\quad \frac{(2hm_1)^{s+1}}{1\,.\,3\,.\,5\ldots(2s+3)\,s}\Delta U_1C_1^{2s}$$
$$= B_0\frac{1}{T}\frac{\partial T}{\partial x}\sum_{r=0}^{\infty}\lambda_{r-1,s-1}\left[\beta_{r-1,1}\{b_{11}(r_1s_1)+b_{12}(r_1s_1)\}+\mu_{12}^{1/2}\beta_{r-1,2}b_{12}(r_2s_1)\right],$$

$$(133)\quad \frac{(2hm_1)^{s+1}}{1\,.\,3\,.\,5\ldots(2s+5)}\Delta U_1^2C_1^{2s} = C_0c_{11}\sum_{r=0}^{\infty}\lambda'_{rs}\left[\gamma_{r,1}\{c_{11}(r_1s_1)+c_{12}(r_1s_1)\}+\gamma_{r,2}c_{12}(r_2s_1)\right].$$

In the present paper we are concerned with the application of these formulæ only to simple gases, in which $\nu_2 = 0$ and hence $b_{12}(r_1s_1) = b_{12}(r_2s_1) = c_{12}(r_1s_1) = c_{12}(r_2s_1) = 0$. It is convenient to write the reduced equations in the following form:—

$$(134)\quad \frac{(2hm)^{s+2}}{1\,.\,3\,.\,5\ldots(2s+5)(s+1)}\frac{3}{\nu}\Delta UC^{2(s+1)} = \frac{1}{T}\frac{\partial T}{\partial x}\sum_{r=0}^{\infty}\beta_r b_{rs},$$

$$(135)\quad \frac{(2hm)^{s+1}}{1\,.\,3\,.\,5\ldots(2s+5)}\frac{45}{2\nu}\Delta U^2C^{2s} = c_{11}\sum_{r=0}^{\infty}\gamma_r c_{rs}.$$

In (134) we have substituted $r+1$, $s+1$ for r, s in (132), multiplied by $3/\nu$, and used the notation given by

$$(136)\quad b_{rs} \equiv \frac{3}{\nu}B_0\lambda_{r,s}b_{11}(r+1, s+1);$$

the first term in (132), with factor β_{-1}, vanishes, since $b_{11}(0, s) = 0$. Similarly in (135) we have written

$$(137)\quad c_{rs} \equiv \frac{45}{2\nu}C_0\lambda'_{rs}c_{11}(r_1s_1).$$

§ 8. THE EXPRESSIONS FOR THE COEFFICIENTS IN THE VELOCITY-DISTRIBUTION FUNCTIONS.

§ 8 (A) We have now obtained expressions for ΔQ, the rate of change of a function of the molecular velocities due to encounters, in two different ways: in § 3 ΔQ was found from the equation of transfer, while in §§ 4–7 it has been determined by direct calculation. By comparison of (26) and (134)—substituting $s+1$ for s in the former —and of (30), (72) and (135), we deduce from these different expressions for ΔQ the following linear equations connecting the unknown coefficients in the velocity-distribution function:—

$$(138) \qquad \sum_{r=0}^{\infty} \beta_r b_{rs} = 1,$$

$$(139) \qquad \sum_{r=0}^{\infty} \gamma_r c_{rs} = 1.$$

These are true for all values of s from 0 to ∞, the coefficients b_{rs} and c_{rs} being completely determined, in terms of the molecular data, by (130), (131),* and (136), (137). If we assume that certain convergency conditions are satisfied (138) and (139) lead (in the way usual in the case of a *finite* system of linear equations) to the following expressions for β_r and γ_r:—

$$(140) \qquad \beta_r = \nabla_r (b_{rs})/\nabla (b_{rs}), \qquad \gamma_r = \nabla_r (c_{rs})/\nabla (c_{rs}),$$

where $\nabla (b_{rs})$ and $\nabla (c_{rs})$ denote the infinite determinants formed from the arrays (b_{rs}) and (c_{rs}), thus,

$$(141) \quad \nabla (b_{rs}) \equiv \begin{vmatrix} b_{00} & b_{10} & b_{20} & b_{30} & . & . \\ b_{01} & b_{11} & b_{21} & b_{31} & . & . \\ b_{02} & b_{12} & b_{22} & b_{32} & . & . \\ b_{03} & b_{13} & b_{23} & c_{33} & . & . \\ . & . & . & . & . & . \end{vmatrix} \qquad \nabla (c_{rs}) \equiv \begin{vmatrix} c_{00} & c_{10} & c_{20} & c_{30} & . & . \\ c_{01} & c_{11} & c_{21} & c_{31} & . & . \\ c_{02} & c_{12} & c_{22} & c_{32} & . & . \\ c_{03} & c_{13} & c_{23} & c_{33} & . & . \\ . & . & . & . & . & . \end{vmatrix}$$

and $\nabla_r (b_{rs})$, $\nabla_r (c_{rs})$ denote the determinants obtained by replacing each element of column (r) in $\nabla (b_{rs})$ and $\nabla (c_{rs})$ respectively by unity.

The General Expression for the Velocity Distribution Function.

§ 8 (B) This completes our solution of the fundamental problem of this paper, *i.e.*, the determination of the velocity-distribution function for a "nearly perfect" simple gas, composed of monatomic molecules of the most general type, and which is slightly non-uniform as regards temperature and mass-velocity. The solution will be summarized as follows (*cf.* (10), (73)):—

$$(142) \quad f(\mathrm{U}, \mathrm{V}, \mathrm{W}) = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)}$$

$$\left\{1 - \mathrm{B}_0 \frac{1}{\mathrm{T}} \left(\mathrm{U}\frac{\partial \mathrm{T}}{\partial x} + \mathrm{V}\frac{\partial \mathrm{T}}{\partial y} + \mathrm{W}\frac{\partial \mathrm{T}}{\partial z}\right) \sum_{r=0}^{\infty} \frac{(2hm)^r}{1.3.5\ldots(2r+3)r} \beta_{r-1} \mathrm{C}^{2r}\right.$$

$$- \mathrm{C}_0 (2hm) (c_{11}\mathrm{U}^2 + c_{22}\mathrm{V}^2 + c_{33}\mathrm{W}^2 + c_{23}\mathrm{VW} + c_{31}\mathrm{WU} + c_{12}\mathrm{UV})$$

$$\left. \sum_{r=0}^{\infty} \frac{(2hm)^r}{1.3.5\ldots(2r+5)} \gamma_r \mathrm{C}^{2r} \right\},$$

---

* The suffix 1 throughout these equations may now be omitted.

where c_{11}, c_{12}, &c., are given by (72). The coefficients β_r and γ_r, for $r = 0$ to $r = \infty$, are given by (140), where (*cf.* (136), (137), (130), (131)),

$$(143)\quad b_{rs} = 32\mathrm{B}_0\nu\lambda_{rs}\iint e^{-(x^2+y^2)}\sum_{k=1}^{[r,\,s]}\phi^{2k}(\tau y)\Big[\mathrm{B}^{2k}(r+2,\,s+1)+\mathrm{B}^{2k}(r+1,\,s+2)$$
$$+2y^2\left\{\frac{2k+1}{4k+1}\,\mathrm{B}^{2k+1}(r+1,\,s+1)+\frac{2k}{4k+1}\,\mathrm{B}^{2k-1}(r+1,\,s+1)\right.$$
$$\left.-\mathrm{B}^{2k}(r+1,\,s+1)\right\}\Big]x^2y^2\,dx\,dy,$$

$$(144)\quad c_{rs} = 72\mathrm{C}_0\nu\lambda'_{rs}\iint e^{-(x^2+y^2)}\sum_{k=1}^{[r,\,s]}\phi^{2k}(\tau y)\Big[\mathrm{B}^{2k}(r+2,\,s)+\tfrac{2}{3}\mathrm{B}^{2k}(r+1,\,s+1)+\mathrm{B}^{2k}(r,\,s+2)$$
$$+4y^2\left\{\frac{2k+1}{4k+1}\Big(\mathrm{B}^{2k+1}(r+1,\,s)+\mathrm{B}^{2k+1}(r,\,s+1)\Big)\right.$$
$$\left.+\frac{2k}{4k+1}\Big(\mathrm{B}^{2k-1}(r+1,s)+\mathrm{B}^{2k-1}(r,s-1)\Big)-\Big(\mathrm{B}^{2k}(r+1,s)+\mathrm{B}^{2k}(r,s+1)\Big)\right\}$$
$$+4y^4\left\{\frac{(2k+2)(2k+1)}{(4k+3)(4k+1)}\mathrm{B}^{2k+2}(r,\,s)\right.$$
$$+\left(\frac{(2k+1)^2}{(4k+3)(4k+1)}+\frac{4k^2}{(4k+1)(4k-1)}+1\right)\mathrm{B}^{2k}(r,\,s)$$
$$+\frac{2k(2k-1)}{(4k+1)(4k-1)}\,\mathrm{B}^{2k-2}(r,\,s)$$
$$\left.-2\left(\frac{2k+1}{4k+1}\,\mathrm{B}^{2k+1}(r,\,s)+\frac{2k}{4k+1}\,\mathrm{B}^{2k-1}(r,\,s)\right)\right\}\Big]x^2y^2\,dx\,dy$$

where (*cf.* (123))

$$(145)\qquad \tau = (2hm)^{-1/2},$$

and, by (111),

$$(146)\qquad \phi^{2k}(z) \equiv 2(4k+1)\,z\int_0^\infty\{1-\mathrm{P}_{2k}(\cos\chi)\}\,p\,dp,$$

where $\mathrm{P}_k(\cos\chi)$ is the usual LEGENDRE'S coefficient, and χ is a function of p and z which depends (§ 4 (D)) on the law of inter-action between two molecules at an encounter. The factors λ_{rs} and λ'_{rs} are defined by (125), (126), while the functions $\mathrm{B}^k(r,\,s)$, which are integral polynomials in x and y, with merely numerical coefficients, are defined by (129) and (96). In the upper limit of k, $[r,\,s]$ denotes the integral part of the lesser of the two quantities $\tfrac{1}{2}r+1$, $\tfrac{1}{2}s+1$.

The factors B_0, C_0 are, as yet, arbitrary; we now assign to them the values determined by the equations

$$(147)\qquad b_{00} = 1,\qquad c_{00} = 1.$$

This makes B_0 and C_0 each equal to ν^{-1} multiplied into a function of $(2hm)$, *i.e.*, of the absolute temperature. The elements b_{rs}, c_{rs} and the coefficients β_r, γ_r then become functions of the temperature only.

The coefficient β_{-1} is not determined by the above equations, but is given (*cf.* (75)) by

$$\beta_{-1} = -\sum_{r=0}^{\infty} \beta_r/(r+1). \tag{148}$$

Properties of the Determinants $\nabla(b_{rs})$, $\nabla(c_{rs})$.

§ 8 (C) On inspection of (143) and (144) it is evident that

$$b_{rs} = b_{sr}, \qquad c_{rs} = c_{sr}, \tag{149}$$

so that $\nabla(b_{rs})$ and $\nabla(c_{rs})$ are *symmetrical* determinants.

In expression (143) for b_{rs}, the variables of integration, x and y, are never negative, so that (*cf.* (129), (96)) ${}^{r}\mathrm{A}^{k}$, ${}^{s}\mathrm{A}^{k}$ and $\mathrm{B}^{k}(r, s)$ are essentially positive (or zero) for all integral values of r, s, and k; further, since $\mathrm{P}_k(\cos\chi)$ never exceeds unity, $\phi^{2k}(\tau y)$ is also always positive. It is evident, therefore, that b_{rs} must be essentially positive if this can be proved true of

$$\mathrm{B}^{2k}(r+2, s+1) - 2y^2\mathrm{B}^{2k}(r+1, s+1) + \mathrm{B}^{2k}(r+1, s+2). \tag{150}$$

Now

$$\begin{aligned}
\mathrm{B}^{2k}(r+2, s+1) - y^2\mathrm{B}^{2k}(r+1, s+1) &= {}^{s+1}\mathrm{A}^{2k}\left[{}^{r+2}\mathrm{A}^{2k} - y^2\,{}^{r+1}\mathrm{A}^{2k}\right] \\
&= {}^{s+1}\mathrm{A}^{2k}\left(\frac{y}{x}\right)^{2k}\left[\sum_{t=2k}^{r+2}\frac{(r+2)_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{5}{2})_{t-2k}}{(t-2k)\,!}x^{2t}y^{2(r+2-t)} - \sum_{t=2k}^{r+1}\frac{(r+1)_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{3}{2})_{t-2k}}{(t+2k)\,!}x^{2t}y^{2(r+2-t)}\right] \\
&= {}^{s+1}\mathrm{A}^{2k}\left(\frac{y}{x}\right)^{2k}\sum_{t=2k}^{r+2}\frac{(r+1)_{t-1}}{(t+\frac{1}{2})_t}\frac{(r+\frac{3}{2})_{t-2k-1}}{(t-2k)\,!}x^{2t}y^{2(r+2-t)}\left\{(r+2-t)(t-2k)+t\left(r+\tfrac{3}{2}\right)\right\},
\end{aligned} \tag{151}$$

every term of which is positive. Interchanging r and s in (151), and adding the result to the latter, we obtain (150), which, with b_{rs} also, in consequence, is essentially positive.

From (151), moreover, it is clear that the numerical coefficients in (151) or (150) increase with r or s, and the same is readily seen to hold good also in the case of $\mathrm{B}^{k}(r, s)$. As r or s increases, therefore, the numerical coefficients and the degree (in x and y) of the integrand of (143) increase, while if both r and s increase, new positive terms are added to the integrand. Hence, provided that the functions $\phi^{2k}(\tau y)$ satisfy certain simple conditions,* b_{rs} steadily increases with r or s, and the consideration of even a single term of (151) or the integrand of (143) shows that this increase is without limit, *i.e.*, b_{rs} tends steadily to infinity with r or s.

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* It is easy to see that the increase with y of $\phi^{2k}(\tau y)$ is less rapid than that of y; if $\phi^{2k}(\tau y)$ is constant or steadily increases, though less rapidly than y, b_{rs} will steadily increase with r or s. But much less restrictive conditions might be devised, *e.g.*, if $\phi^{2k}(\tau y)$ decreases like y^{-1}, the above result still holds good.

I have little doubt that, with rather more trouble, c_{rs} could be shown to share the above properties of b_{rs}, but I have not made any serious attempt to prove this; from the numerical calculations in § 10 (A) it appears probable that the increase of c_{rs} with r, s is more rapid than that of b_{rs}.

Properties of the First Row or Column of $\nabla(b_{rs})$ and $\nabla(c_{rs})$.

§ 8 (D) The numerical values of b_{rs} and c_{rs} obtained in § 10 suggest that many further general properties of these elements might be determined, with sufficient trouble, and that the convergence of the determinants $\nabla(b_{rs})$ and $\nabla(c_{rs})$ might thus be demonstrated. Owing to the considerable algebraic difficulties involved, however, I have so far made little progress towards the proof of such properties, except for the case when r or s is zero, *i.e.*, for the elements of the first row or column of $\nabla(b_{rs})$ and $\nabla(c_{rs})$. It will be shown that

$$b_{r0} = b_{0r} = c_{r0} = c_{0r} \tag{152}$$

for all values of r.

This will be proved as a particular case of the more general result that

(152A) $(s+1)\,b_{rs}(k) = c_{rs}(k)$ when the lesser of r and s is even, and $k = [r, s]$,

where $b_{rs}(k)$, $c_{rs}(k)$ denote the parts of b_{rs} and c_{rs} respectively which are due to a particular value of k in (143), (144), while $[r, s]$ denotes the upper limit of k, as usual, *i.e.*, $k = \frac{1}{2}r+1$ or $\frac{1}{2}s+1$, whichever is the less. Thus if we suppose that $r \geqq s$, and that s is even, (152A) takes the form

$$(s+1)\,b_{rs}(\tfrac{1}{2}s+1) = c_{rs}(\tfrac{1}{2}s+1). \tag{153}$$

When $s = 0$, this value of k is unity, and $b_{r0}(1)$, $c_{r0}(1)$, which usually form only a part of b_{rs}, c_{rs}, become the whole, so that (152) is the particular case of (153) corresponding to this value of s.

Since $\mathrm{B}^k(r, s)$ is zero when either r or s is less than k, some of the terms in $b_{rs}(\frac{1}{2}s+1)$, $c_{rs}(\frac{1}{2}s+1)$ vanish. In fact, as may readily be seen from (143), (144), we have

$$b_{rs}(\tfrac{1}{2}s+1) = 32\mathrm{B}_0\nu\lambda_{rs}\iint e^{-(x^2+y^2)}\phi^{s+2}(\tau y)\left\{\mathrm{B}^{s+2}(r+1, s+2) + \frac{2(s+2)}{2s+5}y^2\mathrm{B}^{s+1}(r+1, s+1)\right\}x^2y^2\,dx\,dy, \tag{154}$$

$$c_{rs}(\tfrac{1}{2}s+1) = 72\mathrm{C}_0\nu\lambda'_{rs}\iint e^{-(x^2+y^2)}\phi^{s+2}(\tau y)\left\{\mathrm{B}^{s+2}(r, s+2) + \frac{4(s+2)}{2s+5}y^2\mathrm{B}^{s+1}(r, s+1) + \frac{4(s+1)(s+2)}{(2s+3)(2s+5)}y^4\mathrm{B}^{s}(r, s)\right\}x^2y^2\,dx\,dy \tag{155}$$

From (96) it is easy to see that

$$(156)\qquad {}^{k}\mathrm{A}^{k} = \frac{k\,!}{(k+\frac{1}{2})_k}(xy)^k,$$

so that

$$(157)\qquad \mathrm{B}^{s+2}(r+1,\ s+2) + \frac{2(s+2)}{2s+5}y^2\mathrm{B}^{s+1}(r+1,\ s+1)$$
$$= \frac{(s+2)\,!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s+1}^{r+1} \frac{(r+1)_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{5}{2})_{t-s-1}}{(t-s-1)\,!}x^{2t}y^{2(r+s+3-t)}.$$

By putting r in place of $(r+1)$ in (157), and adding $\{2(s+2)y^2/(2s+5)\}$ times a similar expression in which r, s replace $r+1$, $s+1$ in (157), we also have

$$(158)\qquad \mathrm{B}^{s+2}(r,\ s+2) + \frac{4(s+2)}{2s+5}y^2\mathrm{B}^{s+1}(r,\ s+1) + \frac{4(s+1)(s+2)}{(2s+3)(2s+5)}y^4\mathrm{B}^{s}(r,\ s)$$
$$= \frac{(s+2)\,!}{(s+\frac{5}{2})_{s+2}} \sum_{t=s}^{r} \frac{r_t}{(t+\frac{1}{2})_t}\frac{(r+\frac{5}{2})_{t-s}}{(t-s)\,!}x^{2t}y^{2(r+s+2-t)}.$$

We now substitute the expressions on the left of (157) and (158) into (154) and (155), and integrate with respect to x by means of the well-known formula

$$(159)\qquad \int_0^\infty e^{-x^2}x^{2(t+1)}\,dx = \tfrac{1}{4}\pi^{1/2}(t+\tfrac{1}{2})_t\,;$$

we thus obtain the equations

$$(160)\quad b_{rs}(\tfrac{1}{2}s+1) = 8\mathrm{B}_0\nu\pi^{1/2}\lambda_{rs}\int e^{-y^2}\phi^{s+2}(\tau y)\frac{(s+2)\,!}{(s+\frac{5}{2})_{s+2}}\sum_{t=s+1}^{r+1}\frac{(r+1)_t(r+\frac{5}{2})_{t-s-1}}{(t-s-1)\,!}y^{2(r+s+4-t)}\,dy,$$

$$(161)\quad c_{rs}(\tfrac{1}{2}s+1) = 18\mathrm{C}_0\nu\pi^{1/2}\lambda'_{rs}\int e^{-y^2}\phi^{s+2}(\tau y)\frac{(s+2)\,!}{(s+\frac{5}{2})_{s+2}}\sum_{t=s}^{r}\frac{r_t(r+\frac{5}{2})_{t-s}}{(t-s)\,!}y^{2(r+s+3-t)}\,dy,$$

or, changing the notation so as to make the lower limit of t zero, and inserting the values of λ_{rs}, λ'_{rs} according to (125), (126), *i.e.*,

$$(162)\qquad \lambda_{rs} = \frac{2^{-(r+s+4)}}{(r+1)(s+1)(r+\frac{5}{2})_{r+2}(s+\frac{5}{2})_{s+2}},\qquad \lambda'_{rs} = \frac{2^{-(r+s+4)}}{(r+\frac{5}{2})_{r+2}(s+\frac{5}{2})_{s+2}},$$

we have

$$(163)\quad b_{rs}(\tfrac{1}{2}s+1)$$
$$= 2^{-(r+s+1)}\mathrm{B}_0\nu\pi^{1/2}\frac{r_s}{(s+1)(r+\frac{5}{2})_{r+2}}\frac{(s+2)\,!}{\{(s+\frac{5}{2})_{s+2}\}^2}\int e^{-y^2}\phi^{s+2}(\tau y)\sum_{t=0}^{r-s}{}_{r-s}\mathrm{C}_t(r+\tfrac{5}{2})_t\,y^{2(r+3-t)}\,dy,$$

$$(164)\quad c_{rs}(\tfrac{1}{2}s+1)$$
$$= 9\,.\,2^{-(r+s+3)}\mathrm{C}_0\nu\pi^{1/2}\frac{r_s}{(r+\frac{5}{2})_{r+2}}\frac{(s+2)\,!}{\{(s+\frac{5}{2})_{s+2}\}^2}\int e^{-y^2}\phi^{s+2}(\tau y)\sum_{t=0}^{r-s}{}_{r-s}\mathrm{C}_t(r+\tfrac{5}{2})_t\,y^{2(r+3-t)}\,dy.$$

The ratio of these two expressions is given by

$$\frac{b_{rs}\left(\frac{1}{2}s+1\right)}{c_{rs}\left(\frac{1}{2}s+1\right)} = \frac{\mathrm{A}}{s+1},$$

where A is a quantity independent of r and s. When $s = 0$, as we have seen, $b_{rs}\left(\frac{1}{2}s+1\right)$ and $c_{rs}\left(\frac{1}{2}s+1\right)$ become identical with b_{rs} and c_{rs} respectively. Hence

$$\frac{b_{r0}}{c_{r0}} = \mathrm{A},$$

and since B_0 and C_0 have been chosen so that $b_{00} = 1$, $c_{00} = 1$, the value of A must be unity. Hence, when s is even and $r \geqq s$,

$$(s+1)\, b_{rs}\left(\tfrac{1}{2}s+1\right) = c_{rs}\left(\tfrac{1}{2}s+1\right),$$

with the consequence that

$$b_{r0} = c_{r0}$$

as a special case.

It is convenient to introduce the notation

$$\int_0^\infty e^{-y^2}\phi^{2k}(\tau y)\, y^{2(m+1)}\, dy \equiv \tfrac{1}{4}\pi^{1/2}\left(m+\tfrac{1}{2}\right)_m \mathrm{K}_{m-2k,\,k}, \tag{165}$$

so that if $\phi^{2k}(\tau y)$ had the value unity, the value of $\mathrm{K}_{m-2k,\,k}$ would also be unity, by (159). In terms of this notation (163) and (164) may be written as follows:—

$$b_{rs}\left(\tfrac{1}{2}s+1\right) = 2^{-(r+s+3)}\,\mathrm{B}_0\nu\pi\frac{r_s}{s+1}\frac{(s+2)\,!}{\left\{\left(s+\frac{5}{2}\right)_{s+2}\right\}^2}\sum_{t=0}^{r-s} {}_{r-s}\mathrm{C}_t \mathrm{K}_{r-s-t,\,\frac{1}{2}s+1}, \tag{166}$$

$$c_{rs}\left(\tfrac{1}{2}s+1\right) = 9\,.\,2^{-(r+s+5)}\,\mathrm{C}_0\nu\pi r_s\frac{(s+2)\,!}{\left\{\left(s+\frac{5}{2}\right)_{s+2}\right\}^2}\sum_{t=0}^{r-s} {}_{r-s}\mathrm{C}_t \mathrm{K}_{r-s-t,\,\frac{1}{2}s+1}. \tag{167}$$

By writing $t = r-s-t'$ it is evident that

$$\sum_{t=0}^{r-s} {}_{r-s}\mathrm{C}_t \mathrm{K}_{r-s-t,\,\frac{1}{2}s+1} = \sum_{t=0}^{r-s} {}_{r-s}\mathrm{C}_t \mathrm{K}_{t,\,\frac{1}{2}s+1}. \tag{168}$$

By giving to r and s in (166), (167) the value zero, we have

$$b_{00} = \tfrac{4}{225}\mathrm{B}_0\nu\pi\mathrm{K}_{0,\,1}, \qquad c_{00} = \tfrac{1}{25}\mathrm{C}_0\nu\pi\mathrm{K}_{01}, \tag{169}$$

whence, remembering that (*cf.* (147)) B_0 and C_0 are so defined as to make b_{00} and c_{00} each equal to unity, we have

$$\mathrm{B}_0 = \tfrac{225}{4}\frac{1}{\pi\nu\mathrm{K}_{0,\,1}}, \qquad \mathrm{C}_0 = 25\frac{1}{\pi\nu\mathrm{K}_{0,\,1}}, \qquad \mathrm{B}_0 = \tfrac{9}{4}\mathrm{C}_0. \tag{170}$$

We will substitute these values into (166), (167), and write $s = 0$, in order to obtain expressions for b_{r0} and c_{r0} as follows :—

(171) $$b_{r0} = b_{0r} = c_{r0} = c_{0r} = \kappa_r/\kappa_0,$$

where we have written

(172) $$\kappa_r \equiv 2^{-r} \sum_{t=0}^{r} {}_rC_t K_{t,1},$$

so that

(173) $$\kappa_0 = K_{0,1} = \frac{16}{15\pi^{1/2}} \int_0^\infty e^{-y^2} \phi^2(\tau y)\, y^6\, dy.$$

It is of interest to examine also the r^{th} successive difference of b_{r0} or c_{r0}, which we shall denote by $\delta_{r0} b_{r0}$ or $\delta_{r0} c_{r0}$. We have

(174) $$\delta_{r0} f(r) = f(r) - {}_rC_1 f(r-1) + {}_rC_2 f(r-2) - \ldots.$$

Then, from (172), it is easy to see that

$$\begin{aligned} \delta_{r0}\kappa_r &= 2^{-r} \sum_{m=0}^{r} (-2)^m {}_rC_m \sum_{t=0}^{r-m} {}_{r-m}C_t K_{t,1} \\ &= 2^{-r} \sum_{t=0}^{r} {}_rC_t K_{t,1} \sum_{m=0}^{r-t} (-2)^m {}_{r-t}C_m \\ &= (-2)^{-r} \sum_{t=0}^{r} (-1)^t {}_rC_t K_{t,1}, \end{aligned}$$

since

$$\sum_{m=0}^{r-t} (-2)^m {}_{r-t}C_m = (1-2)^{r-t} = (-1)^{r-t}.$$

Hence

(175) $$\delta_{r0} b_{r0} = \delta_{r0} c_{r0} = (-2)^{-r} (\kappa_0)^{-1} \sum_{t=0}^{r} (-1)^t {}_rC_t K_{t,1}.$$

Similarly the r^{th} difference of

$$2^{-r} r_s \sum_{t=0}^{r-s} {}_{r-s}C_t K_{t,\frac{1}{2}s+1},$$

which is the part of $b_{rs}(\frac{1}{2}s+1)$ or $c_{rs}(\frac{1}{2}s+1)$ which depends on r (s being even and $r \geqq s$) is equal to

$$(-1)^{r+s} \frac{r_s}{2^r} \sum_{t=0}^{r-s} (-1)^t {}_{r-s}C_t K_{t,\frac{1}{2}s+1}.$$

Symmetrical Expressions for $\sum\limits_{r=0}^{\infty} \beta_r$ *and* $\sum\limits_{r=0}^{\infty} \gamma_r$.

§ 8 (E) While $\nabla(b_{rs})$ and $\nabla(c_{rs})$ are symmetrical, the derived determinants $\nabla_r(b_{rs})$, $\nabla_r(c_{rs})$ are necessarily lacking in symmetry, and our expressions for β_r and γ_r, when we attempt to make successive numerical approximations to their values for particular types of molecular models (*cf.* § 10), appear not to converge at all rapidly. Fortunately, in our applications of the velocity-distribution function to the theory of viscosity and thermal conductivity, we need to know not the individual values of the β's and γ's, but only the sums $\sum\limits_{r=0}^{\infty} \beta_r$ and $\sum\limits_{r=0}^{\infty} \gamma_r$; for these it is possible to determine symmetrical expressions which are found, in practice, to be highly convergent.

In what follows we shall use the symbol δ_{mn} placed before a function of the integral variables r, s (such as b_{rs} or c_{rs}) to denote the $(m, n)^{\text{th}}$ successive difference of this function with respect to r and s respectively. Thus

$$\delta_{m0} f(r, s) = f(r, s) - {}_m\mathrm{C}_1 f(r-1, s) + {}_m\mathrm{C}_2 f(r-2, s) - \ldots$$

$$\delta_{0n} f(r, s) = f(r, s) - {}_n\mathrm{C}_1 f(r, s-1) + {}_n\mathrm{C}_2 f(r, s-2) - \ldots$$

$$\begin{aligned} \delta_{mn} f(r, s) &= \delta_{m0} f(r, s) - {}_n\mathrm{C}_1\, \delta_{m0} f(r, s-1) + {}_n\mathrm{C}_2\, \delta_{m0} f(r, s-2) - \ldots \\ &= \delta_{0n} f(r, s) - {}_m\mathrm{C}_1\, \delta_{0n} f(r-1, s) + {}_m\mathrm{C}_2\, \delta_{0n} f(r-2, s) - \ldots \end{aligned}$$

When we substitute b_{rs} or c_{rs} for $f(r, s)$ in the above formal expressions, any term with a negative suffix is to be omitted as being zero.

Since the value of a determinant is unaltered by subtracting from the elements of any one row or column the corresponding elements of any other row or column, and since this process can be repeated indefinitely often, it is clear that from (141), by subtracting the $(s-1)^{\text{th}}$ row from the s^{th}, for all values of s from 1 onwards, we have*

$$(176) \qquad \nabla(b_{rs}) = \nabla(\delta_{01} b_{rs}), \qquad \nabla(c_{rs}) = \nabla(\delta_{01} c_{rs}).$$

The same process applied to $\nabla_r(b_{rs})$, $\nabla_r(c_{rs})$ leads to determinants identical with $\nabla(\delta_{01} b_{rs})$ and $\nabla(\delta_{01} c_{rs})$ respectively, save that in the r^{th} column all the elements are zero except the one in the first row, which is unity. Evidently, therefore, $\nabla_r(b_{rs})$ and $\nabla_r(c_{rs})$ are the r^{th} minors of determinants which are respectively identical with $\nabla(\delta_{01} b_{rs})$ and $\nabla(\delta_{01} c_{rs})$, except that in each case all the elements of the first row have the value unity. Consequently the sums $\sum\limits_{r=0}^{\infty} \nabla_r(b_{rs})$ and $\sum\limits_{r=0}^{\infty} \nabla_r(c_{rs})$ are equal to the sums of the minors of the two determinants just described, *i.e.*, they are equal to these determinants themselves. Thus, by (140),

$$(177) \qquad \sum_{r=0}^{\infty} \beta_r = \frac{\nabla(\delta_{01} b'_{rs})}{\nabla(\delta_{01} b_{rs})}, \qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla(\delta_{01} c'_{rs})}{\nabla(\delta_{01} c_{rs})},$$

where we have

$$(178) \quad b'_{0s} = 1,\ c'_{0s} = 1,\ (s = 0 \text{ to } \infty), \quad b'_{rs} = b_{rs},\ c'_{rs} = c_{rs},\ (s = 0 \text{ to } \infty,\ r = 1 \text{ to } \infty).$$

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* When $s = 0$, δ_{01} should be replaced by δ_{00}.

To the above determinants we now apply the same process of differencing by columns which has already been applied by rows, and we thus obtain the equations

$$(179)\qquad \sum_{r=0}^{\infty} \beta_r = \frac{\nabla(\delta_{11} b'_{rs})}{\nabla(\delta_{11} b_{rs})}, \qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla(\delta_{11} c'_{rs})}{\nabla(\delta_{11} c_{rs})}.$$

The determinants $\nabla(\delta_{11} b'_{rs})$ and $\nabla(\delta_{11} b_{rs})$ are identical save in their first rows; all the elements of the first row of the former are zero save the first, which is unity. Hence $\nabla(\delta_{11} b'_{rs})$ is equal to the *principal minor* of $\nabla(\delta_{11} b_{rs})$; we shall denote it by $\nabla'(\delta_{11} b_{rs})$. Hence, and with a similar notation for the principal minor of $\nabla(\delta_{11} c_{rs})$, we have*

$$\sum_{r=0}^{\infty} \beta_r = \frac{\nabla'(\delta_{11} b_{rs})}{\nabla(\delta_{11} b_{rs})}, \qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla'(\delta_{11} c_{rs})}{\nabla(\delta_{11} c_{rs})}$$

All these determinants have now regained a symmetrical form.

It is convenient, partly for the sake of elegance, and also because it imparts a highly convergent form to the elements of our determinants (*cf.* § 10) to continue this process of differencing still further, as follows. We repeat the whole of the above operation of differencing by rows and columns an indefinite number of times, beginning now at the second row and column (thus leaving unchanged the values both of ∇ and its principal minor), and afterwards successively at the next later row and column than on the previous occasion. The general element thus becomes $\delta_{rs} b_{rs}$ or $\delta_{rs} c_{rs}$, and we have

$$(180)\qquad \sum_{r=0}^{\infty} \beta_r = \frac{\nabla'(\delta_{rs} b_{rs})}{\nabla(\delta_{rs} b_{rs})}, \qquad \sum_{r=0}^{\infty} \gamma_r = \frac{\nabla'(\delta_{rs} c_{rs})}{\nabla(\delta_{rs} c_{rs})},$$

where the dash (′) denotes the principal minor of the corresponding determinant. These expressions could, of course, have been obtained directly by a re-arrangement of the original equations of transfer, but it seems preferable to use the latter in the more simple, natural forms chosen, and to make this transformation by differencing in relation to the determinants formed by the elements b_{rs}, c_{rs}.

§ 9. CONSIDERATION OF PARTICULAR MOLECULAR MODELS.

§ 9 (A) While, as we have seen, certain general properties of the elements b_{rs}, c_{rs} can be demonstrated without the assumption of any property of the molecules save spherical symmetry, it is possible to carry our investigations much further when we represent the molecules by particular models of simple type, such as point centres of force, or rigid elastic spheres. This involves, primarily, the examination of the functions $\phi^{2k}(\tau y)$.

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* When r or s is zero, the corresponding suffix of δ_{11} should also be written as zero.

Molecules which are Point Centres of Force varying as r^{-n}.

§ 9 (B) When the molecules are point centres of force varying inversely as the n^{th} power of the distance, the angle χ in the expression (146)—*cf.* § 4 (D)—is given by the following integral* :—

$$\chi = 2\int_0^{\eta_0} \left[1-\eta^2-(\eta/\alpha)^{n-1}\right]^{-1/2} d\eta. \tag{181}$$

Here η_0 is the least positive root of the equation $\left[1-\eta^2-(\eta/\alpha)^{n-1}\right] = 0$, and α is a multiple of p, thus,

$$\alpha = p\left(\frac{n-1}{4\mathrm{K}m}\right)^{\frac{1}{n-1}}(2\mathrm{C_R})^{\frac{2}{n-1}} = p\left(\frac{n-1}{\mathrm{K}m}\right)^{\frac{1}{n-1}}\mathrm{C_R}^{\frac{2}{n-1}}, \tag{182}$$

where K is a constant which measures the intensity of force between two molecules at unit distance. Hence (*cf.* (111))

$$\begin{aligned} \phi^{2k}(\tau y) &= 2\,(4k+1)\left(\frac{\mathrm{K}m}{n-1}\right)^{\frac{2}{n-1}}\mathrm{C_R}^{1-\frac{4}{n-1}}\int_0^\infty \{1-\mathrm{P}_{2k}(\cos\chi)\}\,\alpha\,d\alpha \\ &= 2\,(4k+1)\left(\frac{\mathrm{K}m}{n-1}\right)^{\frac{2}{n-1}}\left(\frac{y^2}{2hm}\right)^{\frac{n-5}{2(n-1)}}\int_0^\infty \{1-\mathrm{P}_{2k}(\cos\chi)\}\,\alpha\,d\alpha \\ &= {}_n\mathrm{A}_k\left(\frac{y^2}{2hm}\right)^{\frac{n-5}{2(n-1)}}, \end{aligned} \tag{183}$$

where ${}_n\mathrm{A}_k$ is a constant depending on n and k, but not on y or h (*i.e.*, not on the absolute temperature).

When this value of $\phi^{2k}(\tau y)$ is substituted in our expressions for b_{rs} and c_{rs}, it becomes possible to execute the integration with respect both to x and to y in terms of gamma-functions. Thus (*cf.* (165))

$$\begin{aligned} \int_0^\infty e^{-y^2}\phi^{2k}(\tau y)\,y^{2(m+1)}\,dy &= \tfrac{1}{4}\pi^{1/2}\left(m+\tfrac{1}{2}\right)_m \mathrm{K}_{m-2k,\,k} \\ &= {}_n\mathrm{A}_k\left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}}\int_0^\infty e^{-y^2}y^{2\left(m+1+\frac{1}{2}\frac{n-5}{n-1}\right)}\,dy \\ &= \tfrac{1}{2}\,{}_n\mathrm{A}_k\left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}}\Gamma\left(m+2-\frac{2}{n-1}\right), \end{aligned} \tag{184}$$

so that

$$\kappa_0 = \mathrm{K}_{0,1} = \tfrac{8}{15}\pi^{-1/2}\,{}_n\mathrm{A}_1\left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}}\Gamma\left(4-\frac{2}{n-1}\right) \tag{185}$$

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* *Cf.* § 14, p. 454, of my former memoir, 'Phil. Trans.,' A, vol. 211 (1911). The V_0 of the formula there given is the relative velocity of two molecules, which in our notation is $(\mu_1\mu_2)^{-1/2}\mathrm{C_R} = 2\mathrm{C_R}$ when the gas is simple.

and

$$(186) \qquad \mathrm{K}_{t,1} = 2\pi^{-1/2}{}_n\mathrm{A}_1\left(\frac{1}{2hm}\right)^{\frac{n-5}{2(n-1)}}\{(t+\tfrac{5}{2})_{t+2}\}^{-1}\,\Gamma\left(t+4-\frac{2}{n-1}\right) = \frac{\left(t+3-\frac{2}{n-1}\right)_t}{(t+\frac{5}{2})_t}\mathrm{K}_{0,1}.$$

Hence the values assumed by B_0 and C_0 in this special case are as follows (*cf.* (170), § 8 (D)):—

$$(187) \qquad \mathrm{B}_0 = \frac{15^3}{32}\frac{(2hm)^{1/2\frac{n-5}{n-1}}}{\pi^{1/2}{}_n\mathrm{A}_1\Gamma\left(4-\frac{2}{n-1}\right)\nu}, \qquad \mathrm{C}_0 = \frac{375}{8}\frac{(2hm)^{1/2\frac{n-5}{n-1}}}{\pi^{1/2}{}_n\mathrm{A}_1\Gamma\left(4-\frac{2}{n-1}\right)\nu}.$$

From (186) we have

$$\begin{aligned} b_{r0} = c_{r0} = \kappa_r/\kappa_0 &= 2^{-r}\sum_{t=0}^{r}{}_r\mathrm{C}_t\mathrm{K}_{t,1}/\mathrm{K}_{0,1} \\ &= 2^{-r}\sum_{t=0}^{r}\frac{r_t}{t!}\frac{\left(t+3-\frac{2}{n-1}\right)_t}{(t+\frac{5}{2})_t} \\ &= 2^{-r}\mathrm{F}\left(-r,\ 4-\frac{2}{n-1},\ \tfrac{7}{2},\ -1\right), \end{aligned}$$

in the notation of the hypergeometric function. It may hence be shown, without much difficulty, that (if $n > 5$) b_{r0} and c_{r0} steadily increase to infinity with r, the rate of increase being comparable with that of $r^{\frac{n-5}{n-1}}$.

Since the functions $\phi^{2k}(\tau y)$ all depend on h in the same way, it is clear that, with the above values of B_0 and C_0, the elements b_{rs} and c_{rs} and consequently, also, the coefficients β_r and γ_r in the velocity-distribution function for molecules of this type, are independent of h, *i.e.*, they are independent of temperature. They are, indeed, pure numbers, depending only on the molecular mass and on the force constant of the molecules.

It is of interest to determine the value of the elements $\delta_{r0}b_{r0}$ (or $\delta_{r0}c_{r0}$) of the outer row or column of $\nabla(\delta_{rs}b_{rs})$, in this special case. We have, by (175),

$$\begin{aligned} \delta_{r0}b_{r0} = \delta_{r0}c_{r0} &= (-2)^{-r}\sum_{t=0}^{r}(-1)^t{}_r\mathrm{C}_t\mathrm{K}_{t,1}/\mathrm{K}_{0,1}, \\ &= (-2)^{-r}\sum_{t=0}^{r}(-1)^t\frac{r_t}{t!}\frac{\left(t+3-\frac{2}{n-1}\right)_t}{(t+\frac{5}{2})_t}, \\ &= (-2)^{-r}\mathrm{F}\left(-r,\ 4-\frac{2}{n-1},\ \tfrac{7}{2},\ 1\right), \end{aligned}$$

in the notation of hypergeometric functions, or, in terms of gamma-functions,

$$(188) \qquad \delta_{r0}b_{r0} = \delta_{r0}c_{r0} = (-2)^{-r}\frac{\Gamma(\frac{7}{2})\,\Gamma\left(r-\frac{1}{2}+\frac{2}{n-1}\right)}{\Gamma(r+\frac{7}{2})\,\Gamma\left(\frac{2}{n-1}-\frac{1}{2}\right)} = (-2)^{-r}\frac{\left(r-\frac{3}{2}+\frac{2}{n-1}\right)_r}{(r+\frac{5}{2})_r}.$$

As r tends to infinity, the last expression tends to zero more quickly that

$$2^{-r}r^{-\left(4-\frac{2}{n-1}\right)},$$

and also it is alternately of positive and negative sign, after the first two terms (both $\delta_{00}b_{r0}$ and $\delta_{10}b_{10}$ being positive).

Maxwellian Molecules: $n = 5$.

§ 9 (C) It is now easy to see what are the special properties of the fifth-power law ($n = 5$), the law obeyed by the molecules which we term Maxwellian, which enabled Maxwell to work out the theory on this hypothesis with such great simplicity and accuracy. When $n = 5$, we have from (186)

$$\text{(189)} \qquad \mathrm{K}_{t,1} = {}_5\mathrm{A}_1,$$

which is independent of t. Hence, by (170), (171), (172),

$$\text{(190)} \quad \mathrm{K}_{t,1} = \mathrm{K}_{0,1} = {}_5\mathrm{A}_1, \quad \kappa_r = 2^{-r}\sum_{t=0}^{r} {}_r\mathrm{C}_t\mathrm{K}_{t,1} = 2^{-r}\mathrm{K}_{0,1}\sum_{t=0}^{r} {}_r\mathrm{C}_t = \mathrm{K}_{0,1} = \kappa_0,\ b_{r0} = c_{r0} = 1\,;$$

$$\text{(191)} \qquad \delta_{r,0}b_{r,0} = \delta_{r,0}c_{ro} = (-2)^{-r}\sum_{t=0}^{r}(-1)^t{}_r\mathrm{C}_t = (-2)^{-r}(1-1)^r = 0, \quad (r>0)\,;$$

$$\text{(192)} \qquad \mathrm{B}_0 = \tfrac{225}{4}(\nu_5\mathrm{A}_1)^{-1}, \quad \mathrm{C}_0 = 25\,(\nu_5\mathrm{A}_1)^{-1}.$$

From (191) and the equation $b_{00} = c_{00} = 1$ we deduce that in this case the principal minors of $\nabla(\delta_{rs}b_{rs})$ and $\nabla(\delta_{rs}c_{rs})$ are equal to these determinants themselves, *i.e.*,

$$\text{(193)} \qquad \sum_{r=0}^{\infty}\beta_r = 1, \qquad \sum_{r=0}^{\infty}\gamma_r = 1 \qquad \text{(Maxwellian molecules)},$$

while from (190) it appears that all the elements of the first row and column of $\nabla(b_{rs})$ and $\nabla(c_{rs})$ are unity. Hence in $\nabla_r(b_{rs})$ and $\nabla_r(c_{rs})$ the first column and column (r) are identical, so that we have

$$\left.\begin{array}{lll} \text{(194)} \quad \nabla_r(b_{rs}) = 0, & \nabla_r(c_{rs}) = 0, & r>0 \\ \text{(195)} \quad \nabla_0(b_{rs}) = \nabla(b_{rs}), & \nabla_0(c_{rs}) = \nabla(c_{rs}) & \end{array}\right\} \text{(Maxwellian molecules)},$$

whence also, by (140), we have

$$\text{(196)} \qquad \beta_0 = 1, \qquad \gamma_0 = 1, \qquad \beta_r = \gamma_r = 0, \qquad (r>0) \qquad \text{(Maxwellian molecules)},$$

and also, by (148),

$$\text{(197)} \qquad \beta_{-1} = -\beta_0 = -1 \qquad \text{(Maxwellian molecules)}.$$

In the case of molecules which obey the fifth-power law, therefore, the velocity distribution function has the simple finite form (*cf.* (142))

$$(198)\quad f(\mathsf{U}, \mathsf{V}, \mathsf{W}) = \left(\frac{hm}{\pi}\right)^{3/2} e^{-hm(\mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2)}$$

$$\Big[1-(\nu_5\mathrm{A}_1)^{-1}\Big\{\tfrac{75}{4}\frac{1}{\mathrm{T}}\Big(\mathsf{U}\frac{\partial \mathrm{T}}{\partial x}+\mathsf{V}\frac{\partial \mathrm{T}}{\partial y}+\mathsf{W}\frac{\partial \mathrm{T}}{\partial z}\Big)(-1+\tfrac{1}{5}2hm\mathrm{C}^2)$$

$$+\tfrac{5}{3}(2hm)(c_{11}\mathsf{U}^2+c_{22}\mathsf{V}^2+c_{33}\mathsf{W}^2+2c_{23}\mathsf{VW}+2c_{31}\mathsf{WU}+2c_{12}\mathsf{UV})\Big\}\Big]$$

(Maxwellian molecules),

where $\mathrm{C}^2 = \mathsf{U}^2+\mathsf{V}^2+\mathsf{W}^2$, c_{11}, c_{12}, &c., are given by (72), and (*cf.* (183))

$$(199)\qquad {}_5\mathrm{A}_1 = 10\,(\tfrac{1}{4}\mathrm{K}m)^{1/2}\int_0^\infty \{1-\mathrm{P}_2(\cos\chi)\}\,\alpha\,d\alpha = \tfrac{15}{2}(\mathrm{K}m)^{1/2}\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha.$$

MAXWELL* calculated the value of the integral $\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha$, the forces being repulsive, by numerical quadrature, and found that

$$\pi\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha = 1{\cdot}3682,$$

so that, for repulsive forces proportional to the inverse fifth power of the distance

$$(200)\qquad {}_5\mathrm{A}_1 = \frac{15}{2\pi}\,1{\cdot}3682\,(\mathrm{K}m)^{1/2},$$

where $\mathrm{K}m^2$ is the force between two molecules at unit distance.

Molecules which are Rigid Elastic Spheres.

§ 9 (D) We next consider molecules which behave at encounter like rigid elastic spheres of radius σ. This particular molecular model has been more used than any other, in researches on the kinetic theory, on account of its simplicity and concreteness, which aid the imagination in following or constructing "descriptive" theories of gaseous phenomena. As regards the analytical development of the theory, also, it is probably the simplest case after that of Maxwellian molecules. The difference between the two models in this respect is, however, enormous, the rigid elastic spherical molecule requiring the infinity of terms β_r, γ_r in the velocity-distribution function, just as in the case of the most general molecular model. The comparative simplicity of the present model lies in the moderately tractable expressions for b_{rs}, c_{rs} to which it leads. Apart from the methods of the present and my former paper,

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* MAXWELL, 'Collected Papers,' ii, p. 42. His constant A_2 equals $\pi\int_0^\infty \sin^2\chi\,.\,\alpha\,d\alpha$ in our notation.

however, it has not been found possible in the past to obtain any close numerical accuracy in calculations based on this molecular model, the errors resulting in previous theories (although these have been carefully constructed and closely scrutinized) ranging from 10 to 50 per cent. (*cf.* § 11 (F)).

It is readily seen* that in the present case

$$(201) \qquad \chi = 0 \quad (p > 2\sigma) \qquad \sin \tfrac{1}{2}\chi = p/2\sigma \quad (p \leqq 2\sigma)$$

so that

$$p\,dp = 2\sigma^2 \sin \tfrac{1}{2}\chi \cos \tfrac{1}{2}\chi\, d\chi = \sigma^2 \sin \chi\, d\chi = -\sigma^2\, d \cos \chi.$$

As p ranges from 0 to 2σ, χ ranges from 0 to 2π, and $-\cos \chi$ from -1 to 1.

Hence (*cf.* (111))

$$(202) \qquad \begin{aligned} \phi^{2k}(\tau y) &= 2\,(4k+1)\, \mathrm{C}_{\mathrm{R}} \sigma^2 \int_{-1}^{1} \{1 - \mathrm{P}_{2k}(\cos \chi)\}\, d \cos \chi \\ &= 4\,(4k+1)\, \sigma^2 (2hm)^{-1/2} y, \end{aligned}$$

since $\int_{-1}^{1} \mathrm{P}_{2k}(\mu)\, d\mu = 0$. Hence $\phi^{2k}(\tau y)$ depends on k only as regards the numerical factor $(4k+1)$, and the present case is, analytically, the same as that considered in § 8 (B) if we write (*cf.* (183))

$$(203) \qquad \frac{n-5}{n-1} = 1, \quad \text{or} \quad n = \infty, \quad \text{and} \quad {}_n\mathrm{A}_k = 4\,(4k+1)\,\sigma^2.$$

We may therefore quote from the formulæ of § 8 (B) as follows without further discussion :—

$$(204) \qquad \begin{aligned} \tfrac{1}{4}\pi^{1/2} (m+\tfrac{1}{2})_m \mathrm{K}_{m-2k,\,k} &= 2\,(4k+1)\,\sigma^2 (2hm)^{-1/2} \Gamma(m+2) \\ &= 2\,(4k+1)\,(m+1)!\,\sigma^2 (2hm)^{-1/2}, \end{aligned}$$

$$(205) \qquad \kappa_0 = \mathrm{K}_{0,1} = 64\pi^{-1/2}\sigma^2 (2hm)^{-1/2}, \qquad \mathrm{K}_{t,1} = \mathrm{K}_{0,1}\,(t+3)_t/(t+\tfrac{5}{2})_t.$$

$$(206) \qquad \mathrm{B}_0 = \tfrac{225}{256} \frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2 \nu}, \qquad \mathrm{C}_0 = \tfrac{25}{64} \frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2 \nu},$$

$$(207) \qquad b_{r0} = c_{r0} = 2^{-r} \sum_{t=0}^{r} \frac{r_t}{t!} \frac{(t+3)_t}{(t+\frac{5}{2})_t} = 2^{-r}\mathrm{F}(-r, 4, \tfrac{7}{2}, -1),$$

$$(208) \qquad \delta_{r0} b_{r0} = \delta_{r0} c_{r0} = (-2)^{-r} \frac{(r-\frac{3}{2})_r}{(r+\frac{5}{2})_r} = -(-\tfrac{1}{2})^r \frac{15}{(2r-1)(2r+1)(2r+3)(2r+5)}.$$

As in the case of molecules which are point centres of force varying inversely as

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* *Cf.* § 13, p. 453, of my former paper, 'Phil. Trans.,' A, 211 (1911).

the n^{th} power of the distance, the elements b_{rs} and c_{rs}, and the coefficients β_r and γ_r, are pure numbers, independent of the temperature (*i.e.*, of h).

Molecules which are Rigid Elastic Spheres which Exert Attractive Forces.

§ 9 (E) Experiments on the phenomena of actual gases, as, for example, on the variation of viscosity with temperature, indicate that none of the molecular models so far discussed in this chapter gives a really adequate representation of these phenomena. The best of all the simple models which have been used in the kinetic theory seems to be that considered by VAN DER WAALS and SUTHERLAND, viz., a rigid elastic sphere surrounded by a weak field of attractive force. This agrees with the known fact of slight cohesion in gases. The effect of this field of force on the velocity-distribution function, or on viscosity and thermal conductivity, may be referred mainly to the deflections of molecular paths for which it is responsible *indirectly*, through the collisions which it induces between molecules which would otherwise pass one another without mutual inter-action, rather than to its direct effect in the absence of collisions. The latter effect will be expressly neglected in our calculations, which will therefore be inapplicable to vapours in which the cohesion is large enough to render this neglect invalid.

A detailed account of the dynamics of collisions in these circumstances is given in § 15 of my former paper, from which the following results are quoted. If the potential of the force between two molecules in contact be denoted by $\frac{1}{2}b^2$ (reckoning this potential as zero when the separation is infinite), the condition that a collision may take place is

$$(209) \qquad p < p_0 \quad \text{where} \quad p_0 = 2\sigma\left(1+\frac{b^2}{3\mathrm{C_R}^2}\right)^{1/2}$$

(since the relative velocity, in my former paper written V_0, is here denoted by $2\mathrm{C_R}$). The angle χ corresponding to such a collision is given by

$$(210) \qquad \sin\tfrac{1}{2}\chi = p/p_0.$$

The angle χ corresponding to larger values of p, which do not correspond to actual collisions, is given by (181) if the molecular forces obey the n^{th} power law, but we will here make no assumption on this point, as the deflections produced by the inter-molecular forces alone will be rejected after equation (211). Consequently

$$(211) \quad \phi^{2k}(\tau y) = 2(4k+1)\sigma^2(1+b^2/4\mathrm{C_R}^2)\,\mathrm{C_R}+2(4k+1)\,\mathrm{C_R}\int_{p_0}^{\infty}\{1-\mathrm{P}_{2k}(\cos\chi)\}\,p\,dp$$
$$= 4(4k+1)\sigma^2(2hm)^{-1/2}y\,(1+2hmb^2/4y^2)+f_{2k}(y)$$

by analogy with (202) and (183). The latter term $f_{2k}(y)$ represents the negligible deflecting effect of the forces alone, as above mentioned, and it will be omitted henceforward. Hence, corresponding to the equation (204) of § 9 (D), we have

$$(212) \qquad \tfrac{1}{4}\pi^{1/2}\left(t+\tfrac{1}{2}\right)_t \mathrm{K}_{t-2k,\,k} = 2\,(4k+1)\,\sigma^2\,(2hm)^{-1/2}\,\Gamma\,(t+2)\left(1+\frac{2hmb^2}{4\,(t+1)}\right)$$

$$= 2\,(4k+1)\,(t+1)\,!\,\sigma^2\,(2hm)^{-1/2}\left(1+\frac{3\mathrm{S}}{(t+1)\,\mathrm{T}}\right),$$

where we have written

$$(213) \qquad \mathrm{S} = \frac{b^2m}{12\mathrm{R}}.$$

Similarly we have

$$(214) \qquad \kappa_0 = \mathrm{K}_{0,\,1} = 64\pi^{-1/2}\sigma^2\,(2hm)^{-1/2}\left(1+\frac{\mathrm{S}}{\mathrm{T}}\right),$$

$$(215) \qquad \mathrm{K}_{t,\,1} = 64\pi^{-1/2}\sigma^2\,(2hm)^{-1/2}\,\frac{(t+3)_t}{\left(t+\frac{5}{2}\right)_t}\left(1+\frac{3}{t+3}\,\frac{\mathrm{S}}{\mathrm{T}}\right),$$

$$(216) \qquad \mathrm{B}_0 = \tfrac{225}{256}\,\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu}\,\frac{1}{1+\mathrm{S/T}}, \qquad \mathrm{C}_0 = \tfrac{25}{64}\,\frac{(2hm)^{1/2}}{\pi^{1/2}\sigma^2\nu}\,\frac{1}{1+\mathrm{S/T}}.$$

It will be seen later that S is the well-known "SUTHERLAND'S constant" (§ 11 (F)).

§ 10. NUMERICAL CALCULATIONS FOR PARTICULAR MOLECULAR MODELS.

Rigid Elastic Spheres.

§ 10 (A) In the last section we determined the complete expression for the velocity-distribution function for a gas composed of Maxwellian molecules. In the other cases there considered we must be content to make numerical approximations, which can, of course, be carried to any desired degree of accuracy. We shall consider in most detail the case of rigid elastic spherical molecules, for which we shall calculate b_{rs} and c_{rs} for $0 \leqq r \leqq 3$, $0 \leqq s \leqq 3$. These are chosen for the fullest treatment partly because of their simplicity, and partly as representing the limit between which, and the case of Maxwellian molecules, the molecules of actual gases appear to lie.

In making such numerical approximations the following table of expanded formulæ for $\mathrm{B}^k(r,\,s)$ is useful:—

TABLE I.—Expressions for $\mathrm{B}^k(r,\,s)$.

$$\mathrm{B}^0(0,0) = 1 \quad \mathrm{B}^1(1,1) = \tfrac{2}{3}xy \quad \mathrm{B}^2(2,2) = \tfrac{8}{15}x^2y^2 \quad \mathrm{B}^3(3,3) = \tfrac{16}{35}x^3y^3 \quad \mathrm{B}^4(4,4) = \tfrac{128}{315}x^4y^4$$

$$\mathrm{B}^0(1,\,0) = x^2+y^2 \quad \mathrm{B}^1(2,\,1) = \tfrac{4}{3}xy\,(x^2+y^2) \quad \mathrm{B}^2(3,\,2) = \tfrac{8}{5}xy\,(x^2+y^2)$$

$$\mathrm{B}^3(4,\,3) = \tfrac{64}{35}x^3y^3\,(x^2+y^2) \quad \mathrm{B}^4(5,\,4) = \tfrac{128}{63}x^4y^4\,(x^2+y^2)$$

$$\mathrm{B}^0(2,\,0) = x^4+\tfrac{10}{3}x^2y^2+y^4 \quad \mathrm{B}^1(3,\,1) = 2xy\,(x^4+\tfrac{14}{5}x^2y^2+y^4)$$

$$\mathrm{B}^2(4,\,2) = \tfrac{16}{5}x^2y^2\,(x^4+\tfrac{18}{7}x^2y^2+y^4)$$

$$\mathrm{B}^0(3,\,0) = x^6+7x^4y^2+7x^2y^4+y^6 \quad \mathrm{B}^1(4,\,1) = \tfrac{8}{3}xy\,(x^6+\tfrac{27}{5}x^4y^2+\tfrac{27}{5}x^2y^4+y^6)$$

$$\mathrm{B}^2(5,\,2) = \tfrac{16}{3}x^2y^2\,(x^6+\tfrac{33}{7}x^4y^2+\tfrac{33}{7}x^2y^4+y^6).$$

It is useful also to recall that $B^k(r, s) = B^k(s, r)$, and that $B^k(r, s) = 0$ if $r < k$ or $s < k$.

By using these formulæ in connection with (143), (144), (147) and (204)–(208) the elements b_{rs}, c_{rs}, have been calculated,* as above mentioned, and are given in the following expressions :—

$$(217) \qquad \nabla(b_{rs}) = \left|\begin{array}{ccccc} 1 & \frac{15}{2.7} & \frac{41}{2^2 3^2} & \frac{741}{2^3 7.11} & \cdot\ \cdot \\ \frac{15}{2.7} & \frac{269}{2^2 7^2} & \frac{5993}{2^3 3^2 7^2} & \frac{7571}{2^4 3.7.11} & \cdot\ \cdot \\ \frac{41}{2^2 3^2} & \frac{5993}{2^3 3^2 7^2} & \frac{152537}{2^4 3^4 7^2} & \frac{1517873}{2^5 3^3 7^2 11} & \cdot\ \cdot \\ \frac{741}{2^3 7.11} & \frac{7571}{2^4 3.7.11} & \frac{1517873}{2^5 3^3 7^2 11} & \frac{50375871}{2^6 3^3 7^2 11^2} & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

$$(218) \qquad \nabla(c_{rs}) = \left|\begin{array}{ccccc} 1 & \frac{15}{2.7} & \frac{41}{2^2 3^2} & \frac{741}{2^3 7.11} & \cdot\ \cdot \\ \frac{15}{2.7} & \frac{877}{2^2 3.7^2} & \frac{6893}{2^3 3^2 7^2} & \frac{3889}{2^4 3^2 11} & \cdot\ \cdot \\ \frac{41}{2^2 3^2} & \frac{6893}{2^3 3^2 7^2} & \frac{193329}{2^4 3^4 7^2} & \frac{6202777\frac{2}{7}}{2^5 3^4 7^2 11} & \cdot\ \cdot \\ \frac{741}{2^3 7.11} & \frac{3889}{2^4 3^2 11} & \frac{6202777\frac{2}{7}}{2^5 3^4 7^2 11} & \frac{225937695}{2^6 3^4 7^2 11^2} & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

or, writing out the elements in decimals to six places,

$$(219) \qquad \nabla(b_{rs}) = \left|\begin{array}{ccccc} 1\cdot000{,}000 & 1\cdot071{,}429 & 1\cdot138{,}889 & 1\cdot202{,}922 & \cdot\ \cdot \\ 1\cdot071{,}429 & 1\cdot372{,}449 & 1\cdot698{,}696 & 2\cdot048{,}431 & \cdot\ \cdot \\ 1\cdot138{,}889 & 1\cdot698{,}696 & 2\cdot402{,}006 & 3\cdot259{,}364 & \cdot\ \cdot \\ 1\cdot202{,}922 & 2\cdot048{,}431 & 3\cdot259{,}364 & 4\cdot916{,}968 & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

$$(220) \qquad \nabla(c_{rs}) = \left|\begin{array}{ccccc} 1\cdot000{,}000 & 1\cdot071{,}429 & 1\cdot138{,}889 & 1\cdot202{,}922 & \cdot\ \cdot \\ 1\cdot071{,}429 & 1\cdot491{,}497 & 1\cdot953{,}798 & 2\cdot455{,}177 & \cdot\ \cdot \\ 1\cdot138{,}889 & 1\cdot953{,}798 & 3\cdot044{,}359 & 4\cdot439{,}790 & \cdot\ \cdot \\ 1\cdot202{,}922 & 2\cdot455{,}177 & 4\cdot439{,}790 & 7\cdot350{,}929 & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

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* A considerable part of the computations of § 10 (A) have been made by Mr. J. MARSHALL, Scholar of Trinity College, Cambridge, who has thus been of much assistance in bringing the results into a useful form.

As explained in § 8 (E), however, the determinants $\nabla(\delta_{rs}b_{rs})$ and $\nabla(\delta_{rs}c_{rs})$ derived from the above by successive differencing are much more useful and suitable for numerical calculation.* They may conveniently be written as follows, where the factor above each column or before each row is to be multiplied into all the elements of that column or row as written (*e.g.*, the right-hand element on the second row of $\nabla(\delta_{rs}b_{rs})$ is equal to $-59 \,.\, \{2^3 3.7.11.2.7\}^{-1}$):—

$$(221) \qquad \nabla(\delta_{rs}b_{rs}) = \begin{array}{r|rrrrr} & 1 & (2.7)^{-1} & (2^2 3^2 7)^{-1} & (2^3 3.7.11)^{-1} & \\ \hline 1 & 1 & 1 & -1 & 1 & \cdot\ \cdot \\ (2.7)^{-1} & 1 & 45 & 103 & -59 & \cdot\ \cdot \\ (2^2 3^2 7)^{-1} & -1 & 103 & 5657 & 6783 & \cdot\ \cdot \\ (2^3 3.7.11)^{-1} & 1 & -59 & 6783 & 149749 & \cdot\ \cdot \\ & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot \end{array}$$

$$(222) \qquad \nabla(\delta_{rs}c_{rs}) = \begin{array}{r|rrrrr} & 1 & (2.7)^{-1} & (2^2 3^2 7)^{-1} & (2^3 3.7.11)^{-1} & \\ \hline 1 & 1 & 1 & -1 & 1 & \cdot\ \cdot \\ (2.7)^{-1} & 1 & \frac{205}{3} & 163 & -\frac{287}{3} & \cdot\ \cdot \\ (2^2 3^2 7)^{-1} & -1 & 163 & 11889 & 16798\frac{3}{7} & \cdot\ \cdot \\ (2^3 3.7.11)^{-1} & 1 & -\frac{287}{3} & 16798\frac{3}{7} & 329573\frac{10}{21} & \cdot\ \cdot \\ & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot \end{array}$$

As we are throughout concerned with ratios of determinants, the above fractional expressions for the elements, from which the column-factors or row-factors can for many purposes be omitted, are the most suitable for calculation. The following values of the elements in decimal notation (to six places) are of interest, however, as showing the relative magnitudes of the various terms :—

$$(223) \qquad \nabla(\delta_{rs}b_{rs}) = \left|\begin{array}{rrrrr} 1{\cdot}000,000 & 0{\cdot}071,429 & -0{\cdot}003,968 & 0{\cdot}000,541 & \cdot\ \cdot \\ 0{\cdot}071,429 & 0{\cdot}229,592 & 0{\cdot}029,195 & -0{\cdot}002,280 & \cdot\ \cdot \\ -0{\cdot}003,968 & 0{\cdot}029,195 & 0{\cdot}089,081 & 0{\cdot}014,565 & \cdot\ \cdot \\ 0{\cdot}000,541 & -0{\cdot}002,280 & 0{\cdot}014,565 & 0{\cdot}043,849 & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

$$(224) \qquad \nabla(\delta_{rs}c_{rs}) = \left|\begin{array}{rrrrr} 1{\cdot}000,000 & 0{\cdot}071,429 & -0{\cdot}003,968 & 0{\cdot}000,541 & \cdot\ \cdot \\ 0{\cdot}071,429 & 0{\cdot}348,639 & 0{\cdot}046,202 & -0{\cdot}003,698 & \cdot\ \cdot \\ -0{\cdot}003,968 & 0{\cdot}046,202 & 0{\cdot}187,216 & 0{\cdot}036,072 & \cdot\ \cdot \\ 0{\cdot}000,541 & -0{\cdot}003,698 & 0{\cdot}036,072 & 0{\cdot}096,504 & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

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[*] This process of differencing renders the determinants much more convergent in appearance (*cf.* (219) and (220) with (223) and (224), without really altering in the least their value or the value of any of the partial determinants formed by the first n rows and columns.

By taking these determinants with one, two, three, and four columns we get successive approximations to ∇, ∇' (*cf.* § 8 (E)), and to the actual coefficients β and γ, as follows :—

TABLE II.—Rigid Elastic Spheres.

	$\nabla(b_{rs})$.	$\nabla(c_{rs})$.	$\Sigma\beta_r = \dfrac{\nabla'(\delta_{rs}b_{rs})}{\nabla(\delta_{rs}b_{rs})}$.	$\Sigma\gamma_r = \dfrac{\nabla'(\delta_{rs}c_{rs})}{\nabla(\delta_{rs}c_{rs})}$.
1st approximation	1·000,00	1·000,00	1·000,000	1·000,000
2nd ,,	0·224,49	0·343,54	1·022,727	1·014,851
3rd ,,	0·019,13	0·062,15	1·024,818	1·015,879
4th ,,	0·000,79	0·005,54	1·025,134	1·016,065

The determinants $\nabla(\delta_{rs}b_{rs})$, $\nabla(\delta_{rs}c_{rs})$ are obviously much more convergent in form than $\nabla(b_{rs})$, $\nabla(c_{rs})$. Table II. shows that in each case these determinants converge rapidly to the value zero, but that the principal minors of the former determinants converge also to the same value in nearly constant ratios. These ratios, the successive approximations to which are given in the two last columns of Table II., are the quantities $\Sigma\beta_r$ and $\Sigma\gamma_r$ which we require ; they evidently converge rapidly, the successive differences being as follows :—

TABLE III.—Rigid Elastic Spheres.

	$\Sigma\beta_r$.	Differences.	$\Sigma\gamma_r$.	Differences.
1st approximation	1·000,00		1·000,00	
		2273		1485
2nd ,,	1·022,73		1·014,85	
		209		103
3rd ,,	1·024,82		1·015,88	
		31		29
4th ,,	1·025,13		1·016,07	

We may therefore conclude that, within a small fraction per cent., $\Sigma\beta_r$ and $\Sigma\gamma_r$ have the following values for rigid elastic spheres :—

$$(225) \qquad \sum_0^\infty \beta_r = 1\cdot026, \quad \sum_0^\infty \gamma_r = 1\cdot016, \quad \sum_0^\infty \beta_r \Big/ \sum_0^\infty \gamma_r = 1\cdot010.$$

It should be noticed that even the second approximations to these quantities give results which are very nearly accurate, owing to the rapid diminution of the successive differences.

While we may thus obtain a close approximation to the values of the series $\Sigma\beta_r$ and $\Sigma\gamma_r$ with little difficulty, the approximations to the values of the individual coefficients β and γ converge by no means quickly, as the following table shows:—

TABLE IV.—Rigid Elastic Spheres.

	1st approximation.	2nd approximation.	3rd approximation.	4th approximation.
β_0	1·000,0	1·340,9	1·520,2	1·623,0
β_1	—	−0·318,2	−0·652,1	−0·943,2
β_2	—	—	0·156,7	0·432,8
β_3	—	—	—	−0·087,5
γ_0	1·000,0	1·222,8	1·309,4	1·366,3
γ_1	—	−0·207,9	−0·368,8	−0·526,3
γ_2	—	—	0·075,4	0·221,8
γ_3	—	—	—	−0·045,7

Evidently the β's and γ's alternate in sign, and successive terms do not seem to diminish quickly, at any rate near the beginning. To obtain an accurate estimate of the real values of these coefficients it is clearly necessary to carry the approximation much further than we have done, but for our purpose this is not required.

Molecules which are Point Centres of Force varying as r^{-n}.

§ 10 (B) The next simplest case, analytically, to that which has just been discussed is the case of molecules which are point centres of force varying inversely as the n^{th} power of the distance. By comparison of (186) and (205), in conjunction with the general expressions for b_{rs} and c_{rs}, it is easy to see that the difference between the values of b_{rs} or c_{rs} in the two cases consists of a power series in $\frac{1}{n-1}$, the constant term of which is zero, while the term of highest order is $(n-1)^{-(r+s)}$. Numerically the difference is small, as may easily be verified in any particular case; it appears to be of constant sign, b_{rs} and c_{rs} being greatest for molecules which are rigid elastic spheres. The behaviour of the determinants $\nabla(b_{rs})$, $\nabla(c_{rs})$ or $\nabla(\delta_{rs}b_{rs})$, $\nabla(\delta_{rs}c_{rs})$ is similar in the two cases, the convergence being slightly the more rapid in the present instance. Since for rigid elastic spheres the second approximation to $\Sigma\beta_r$ and $\Sigma\gamma_r$ proved so satisfactory, we shall be content with a second approximation only, for molecules which are point centres of force; this very materially lightens the labour of numerical calculation. The following are the expressions found for the determinants $\nabla(\delta_{rs}b_{rs})$, $\nabla(\delta_{rs}c_{rs})$ as far as regards the first four elements:—

$$(226)\quad \nabla(\delta_{rs}b_{rs}) = \left|\begin{array}{ccc} 1 & \left\{\frac{1}{14}-\frac{7}{2(n-1)}\right\} & \cdot\ \cdot \\ \left\{\frac{1}{14}-\frac{7}{2(n-1)}\right\} & \left\{\frac{45}{196}-\frac{4}{49(n-1)}+\frac{4}{49(n-1)^2}\right\} & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|$$

$$\nabla(\delta_{rs}c_{rs}) = \left|\begin{array}{ccc} 1 & \left\{\frac{1}{14}-\frac{7}{2(n-1)}\right\} & \cdot\ \cdot \\ \left\{\frac{1}{14}-\frac{7}{2(n-1)}\right\} & \left\{\frac{205}{588}-\frac{4}{49(n-1)}+\frac{4}{49(n-1)^2}\right\} & \cdot\ \cdot \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \cdot\ \cdot \end{array}\right|.$$

When n is made infinite these become identical with (221), (222); it is interesting to notice that the additional terms are the same in the two determinants, though whether this is true for other values of r and s is not clear.

The first approximations to $\Sigma\beta_r$, $\Sigma\gamma_r$ are, of course, unity; the second are found to be approximately as follows:—

$$(227)\qquad \Sigma\beta_r = \frac{45}{44}\,\frac{1-\frac{16}{45}\frac{n-2}{(n-1)^2}}{1-\frac{2}{11}\frac{1}{n-1}}, \qquad \Sigma\gamma_r = \frac{205}{202}\,\frac{1-\frac{48}{205}\frac{n-2}{(n-1)^2}}{1-\frac{12}{101}\frac{1}{n-1}}.$$

From § 9 (C), (196), we know that when $n = 5$ the values of $\sum\limits_0^\infty\beta_r$ and $\sum\limits_0^\infty\gamma_r$ are unity, and this is also true of any approximation to their values made in the present manner. From § 10 (A), however, we know that for $n = \infty$ the second approximations are slightly too small, by 0·003 and 0·001 very nearly. In the following table, therefore, which gives the approximate values of $\Sigma\beta_r$ and $\Sigma\gamma_r$ for various values of n lying between 5 and ∞, the results obtained from (227) have been increased by 0·001, 0·002, or 0·003, as seemed most appropriate in each case.

TABLE V.—Molecules which are Point Centres of Force varying as r^{-n}.

	MAXWELL'S case, $n = 5$.	$n = 9$.	$n = 15$.	$n = 25$.	$n = \infty$, rigid elastic spheres.
$\sum\limits_0^\infty\beta_r$	1	1·007	1·013	1·018	1·026
$\epsilon_c \equiv \sum\limits_0^\infty\gamma_r$	1	1·004	1·007	1·011	1·016
$\delta_c \equiv \sum\limits_0^\infty\beta_r/\sum\limits_0^\infty\gamma_r$	1	1·003	1·006	1·007	1·010

Rigid Elastic Attracting Spherical Molecules.

§ 10 (C) Considering next the case of rigid elastic spherical molecules which exert attractive forces, as in § 9 (E), we shall neglect the effect of the attractions in producing deflections without actual collisions, and, as in § 10 (B), we shall content ourselves with a second approximation to $\Sigma\beta_r$ and $\Sigma\gamma_r$. The difference between this case and that of rigid elastic spheres without attraction is small. The expressions for $\nabla(\delta_{rs}b_{rs})$ $\nabla(\delta_{rs}c_{rs})$, as far as regards the first four elements, are as follows :—

(228)
$$\nabla(\delta_{rs}b_{rs}) = \left|\begin{array}{ccc} 1 & \left\{\frac{1}{14}\,\frac{1-\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \cdot\;\cdot \\ \left\{\frac{1}{14}\,\frac{1-\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \left\{\frac{45}{196}\,\frac{1+\frac{3}{5}\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \end{array}\right|$$

$$\nabla(\delta_{rs}c_{rs}) = \left|\begin{array}{ccc} 1 & \left\{\frac{1}{14}\,\frac{1-\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \cdot\;\cdot\;\cdot \\ \left\{\frac{1}{14}\,\frac{1-\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \left\{\frac{205}{588}\,\frac{1+\frac{193}{205}\mathrm{S/T}}{1+\mathrm{S/T}}\right\} & \cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot & \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot & \end{array}\right|.$$

When S = 0, *i.e.*, when there is no attraction, these reduce to (221), (223).

The second approximations to $\Sigma\beta_r$ and $\Sigma\gamma_r$ are hence found to be as follows :—

(229)
$$\sum_0^\infty \beta_r = \frac{45\,(1+\frac{3}{5}\mathrm{S/T})}{45\,(1+\frac{3}{5}\mathrm{S/T})-(1-\mathrm{S/T})^2\,(1+\mathrm{S/T})^{-1}}, \text{ approximately,}$$

(230)
$$\sum_0^\infty \gamma_r = \frac{205\,(1+\frac{193}{205}\mathrm{S/T})}{205\,(1+\frac{193}{205}\mathrm{S/T})-3\,(1-\mathrm{S/T})^2\,(1+\mathrm{S/T})^{-1}}, \text{ approximately.}$$

Since S/T is never negative, it is clear from (229), (230) that the second approximations to $\Sigma\beta_r$ and $\Sigma\gamma_r$ are never less than unity. Their values, without any estimated correction for the error of approximation, are given in the following table, for various values of S/T. The correction as estimated is appended as a suffix, and is to be added to the last digit of the corresponding number.

TABLE VI.—Rigid Elastic Attracting Spherical Molecules.

	Low temperatures.					Moderate temperatures.			High temperatures.		
$\frac{\mathrm{S}}{\mathrm{T}}$.	∞.	5.	4.	3.	2.	1.	0·7.	0·4.	0·2.	0·1.	0.
$\sum\limits_0^\infty \beta_r$	1·038	$1{\cdot}015_2$	$1{\cdot}012_2$	$1{\cdot}008_1$	$1{\cdot}004_0$	1	$1{\cdot}001_0$	$1{\cdot}005_1$	$1{\cdot}011_2$	$1{\cdot}016_2$	$1{\cdot}023_3$
$\epsilon_a \equiv \sum\limits_0^\infty \gamma_r$.	1·016	$1{\cdot}009_1$	$1{\cdot}007_1$	$1{\cdot}005_1$	$1{\cdot}002_0$	1	$1{\cdot}001_0$	$1{\cdot}004_0$	$1{\cdot}009_1$	$1{\cdot}013_1$	$1{\cdot}015_1$
$\delta_a \equiv \sum\limits_0^\infty \beta_r / \sum\limits_0^\infty \gamma_r$	1·022	$1{\cdot}006_1$	$1{\cdot}005_1$	$1{\cdot}003_0$	$1{\cdot}002_0$	1	$1{\cdot}000_0$	$1{\cdot}001_1$	$1{\cdot}002_1$	$1{\cdot}003_1$	$1{\cdot}008_2$

In the case of the actual gases for which S has been determined, it has an extreme range from about 50 to 250, while the range of absolute temperature over which experiments are usually made is from about 50° C. to 500° C. Thus the limits 5 and $\frac{1}{5}$ are rather extreme values of S/T, but from the above table it appears that the variation in $\Sigma\beta_r$, $\Sigma\gamma_r$ or their quotient hardly exceeds ·1 per cent. over this range. The variation is especially slow in the neighbourhood of S/T = 1.

§ 11. Viscosity and Thermal Conduction.

We now proceed to apply the expression for the velocity-distribution function (§ 8 (B)) to the determination of the coefficients of viscosity and thermal conduction. We shall first obtain general formulæ for these coefficients, true for any monatomic gas, afterwards considering special molecular models in conjunction with the results of §§ 9, 10.

The Coefficient of Viscosity.

§ 11 (A) The system of pressures at any point of a gas is given by the equation

(231) $$\mathrm{P}_{xx} = \rho\overline{\mathsf{U}^2}, \quad \mathrm{P}_{xy} = \rho\overline{\mathsf{UV}}, \text{ \&c.}$$

By means of (5) and the velocity-distribution function (142), we find that

(232) $$\begin{aligned}\mathrm{P}_{xx} &= \rho\overline{\mathsf{U}^2} = \tfrac{1}{3}\rho\overline{\mathrm{C}^2}+\tfrac{1}{3}\rho\overline{3\mathsf{U}^2-\mathrm{C}^2},\\ &= \frac{\rho}{2hm}-\frac{\rho}{15hm}c_{11}\mathrm{C}_0\sum_0^\infty\gamma_r.\end{aligned}$$

(233) $$\mathrm{P}_{xy} = -\frac{\rho}{30hm}c_{12}\mathrm{C}_0\sum_0^\infty\gamma_r.$$

Since, by (74),

$$c_{11}+c_{22}+c_{33} = 0,$$

we have

(234) $$\mathrm{P}_{xx}+\mathrm{P}_{yy}+\mathrm{P}_{zz} = 3\frac{\rho}{2hm} = p,$$

p being the hydrostatic pressure as usually defined.

By comparing (232), (233) with the equations giving the system of pressures in a viscous fluid having a coefficient of viscosity μ, viz., with

(235) $$\begin{aligned}\mathrm{P}_{xx} &= p-\tfrac{2}{3}\mu\left(2\frac{\partial u_0}{\partial x}-\frac{\partial v_0}{\partial y}-\frac{\partial w_0}{\partial z}\right),\\ &= p-\tfrac{2}{3}\mu c_{11}.\end{aligned}$$

(236) $$\mathrm{P}_{xy} = -\mu\left(\frac{\partial v_0}{\partial x}+\frac{\partial u_0}{\partial y}\right) = -\tfrac{1}{3}\mu c_{12}$$

(remembering the meaning of c_{11}, c_{12}, &c., as defined in (72)), it appears that the two are identical if we write

(237) $$\mu = \tfrac{1}{10}\frac{\rho}{hm}\mathrm{C}_0\sum_0^\infty \gamma_r.$$

Hence, according to the kinetic theory, a gas behaves like an ordinary viscous fluid having a coefficient of viscosity defined in terms of the molecular data by (237).

By (170), (173) we have

(238) $$\mathrm{C}_0 = \frac{25}{\pi\nu\kappa_0},$$

whence, also,

(239) $$\mu = \frac{5}{2\pi}\frac{1}{h\kappa_0}\sum_0^\infty \gamma_r.$$

As we have seen in § 8 (B), κ_0 and $\sum_0^\infty \gamma_r$ are functions of the temperature (or h) only, and ν does not appear at all in the formula for μ. Hence, within the limits of applicability of our theory (*cf.* § 2), the coefficient of viscosity of a gas is independent of its density, varying only with the temperature. The law of this variation depends on the law of inter-action between two molecules at encounter, this being involved through $\phi^k(\tau y)$. As this function has remained unspecified, the expression in (237) is perfectly general and valid for any nearly perfect monatomic gas.

The Equation of Energy for a Simple Monatomic Gas.

§ 11 (B) In the discussion of the equation of transfer in § 3, we consistently neglected such second order quantities as products of differentials, or differentials of small quantities like $\overline{\mathsf{UV}}$, $\overline{\mathrm{C}^2-3\mathsf{U}^2}$, and so on. In this way we have obtained an expression for the velocity-distribution function which is correct to the first order. By means of this function we can now determine the values of $\overline{\mathsf{UV}}$, $\overline{\mathrm{C}^2-3\mathsf{U}^2}$, $\overline{\mathsf{U}\mathrm{C}^2}$, and similar expressions which are of the first order of small quantities, and by substitution in the equation of transfer obtain this in a form accurate to the second order. This we shall do for the special case $\mathrm{Q} = (u)^2+(v)^2+(w)^2$, in order to get a second approximation to the equation of energy.

From the velocity-distribution function, using the formula (237) for the coefficient of viscosity, we have

(240) $$\mathrm{C}^2 = 3\,(hm)^{-1} = 3\mathrm{R}_\nu\mathrm{T}/m.$$

(241) $$\overline{3\mathsf{U}^2-\mathrm{C}^2} = -2\,(\mu/\rho)\left(2\frac{\partial u_0}{\partial x} - \frac{\partial v_0}{\partial y} - \frac{\partial w_0}{\partial z}\right)$$

(242) $$\overline{\mathsf{UV}} = -(\mu/\rho)\left(\frac{\partial v_0}{\partial x} + \frac{\partial u_0}{\partial y}\right).$$

In finding $\overline{\mathsf{U}\mathrm{C}^2}$ it is convenient to write

(243) $$f = \tfrac{5}{2}\sum_0^\infty \beta_r \Big/ \sum_0^\infty \gamma_r$$

and to recall (*cf.* (170)) that

(244) $$\mathrm{B}_0 = \tfrac{9}{4}\mathrm{C}_0.$$

Thus we have

(245) $$\overline{\mathsf{U}\mathrm{C}^2} = -\tfrac{2}{3}\mathrm{B}_0\,(2hm)^{-2}\frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x}\sum_0^\infty \frac{r+\frac{5}{2}}{r}\,\beta_{r-1}$$

$$= -\tfrac{2}{3}\mathrm{B}_0\,(2hm)^{-2}\frac{1}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial x}\sum_0^\infty \beta_r = -3f\frac{\mu}{\rho}\frac{\mathrm{R}}{m}\frac{\partial \mathrm{T}}{\partial x},$$

where we have eliminated β_{-1} by means of (148).

Again, if $\mathrm{Q} = (u)^2+(v)^2+(w)^2$, we have

$$\mathrm{Q} = u_0^2+v_0^2+w_0^2+2\,(u_0\mathsf{U}+v_0\mathsf{V}+w_0\mathsf{W})+\mathrm{C}^2,$$

$$\overline{\mathrm{Q}} = u_0^2+v_0^2+w_0^2+\overline{\mathrm{C}^2},$$

$$\overline{(u)\,\mathrm{Q}} = u_0\,(u_0^2+v_0^2+w_0^2)+u_0\overline{\mathrm{C}^2}+2\,(u_0\overline{\mathsf{U}^2}+v_0\overline{\mathsf{U}\mathsf{V}}+w_0\overline{\mathsf{U}\mathsf{W}})+\overline{\mathsf{U}\mathrm{C}^2}.$$

$$\frac{\partial \mathrm{Q}}{\partial\,(u)} = (u), \qquad \left(\overline{\frac{\partial \mathrm{Q}}{\partial\,(u)}}\right) = u_0.$$

Hence, putting $u_0 = v_0 = w_0 = 0$ except in differential coefficients, we have

$$\frac{\partial}{\partial t}(\nu\overline{\mathrm{Q}}) = 3\frac{\partial}{\partial t}\left(\frac{\nu}{2hm}\right) = \frac{3}{2hm}\frac{\partial \nu}{\partial t}+3\nu\frac{\partial}{\partial t}\left(\frac{1}{2hm}\right)$$

$$= -3\frac{\mathrm{R}\nu\mathrm{T}}{m}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)+3\frac{\mathrm{R}\nu}{m}\frac{\partial \mathrm{T}}{\partial x}.$$

$$\Sigma\frac{\partial}{\partial x}\left(\nu\,\overline{(u)\,\mathrm{Q}}\right) = \nu\Sigma\left(\overline{\mathrm{C}^2+2\mathsf{U}^2}\frac{\partial u_0}{\partial x}+2\overline{\mathsf{U}\mathsf{V}}\frac{\partial v_0}{\partial x}+2\overline{\mathsf{U}\mathsf{W}}\frac{\partial w_0}{\partial x}\right)+\Sigma\frac{\partial}{\partial x}(\nu\overline{\mathsf{U}\mathrm{C}^2})$$

$$= \nu\Sigma\left\{\tfrac{5}{3}\overline{\mathrm{C}^2}\frac{\partial u_0}{\partial x}+\tfrac{2}{3}\,\overline{3\mathsf{U}^2-\mathrm{C}^2}\frac{\partial u_0}{\partial x}+2\overline{\mathsf{U}\mathsf{V}}\frac{\partial v_0}{\partial x}+2\overline{\mathsf{U}\mathsf{W}}\frac{\partial w_0}{\partial x}\right\}+\Sigma\frac{\partial}{\partial x}(\nu\overline{\mathsf{U}\mathrm{C}^2})$$

$$= 5\frac{\mathrm{R}\nu\mathrm{T}}{m}\left(\frac{\partial u_0}{\partial x}+\frac{\partial v_0}{\partial y}+\frac{\partial w_0}{\partial z}\right)$$

$$-\frac{\mu}{\rho}\left\{4\Sigma\left(\frac{\partial u_0}{\partial x}\right)^2-\tfrac{4}{3}\left(\Sigma\frac{\partial u_0}{\partial x}\right)^2-2\Sigma\left(\frac{\partial v_0}{\partial z}+\frac{\partial w_0}{\partial y}\right)^2\right\}+\Sigma\frac{\partial}{\partial x}(\nu\overline{\mathsf{U}\mathrm{C}^2}),$$

$$\frac{\nu}{m}\Sigma\mathrm{X}\left(\overline{\frac{\partial \mathrm{Q}}{\partial\,(u)}}\right) = 0.$$

Also, since no energy is gained or lost in molecular encounters,

$$\Delta\mathrm{Q} = 0.$$

The equation of transfer becomes, consequently, after a little reduction,

$$(246)\qquad \rho\frac{\partial \mathrm{T}}{\partial t} = \Sigma\frac{\partial}{\partial x}\left(f\mu\frac{\partial \mathrm{T}}{\partial x}\right) - \tfrac{2}{3}\rho\mathrm{T}\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right)$$
$$+\tfrac{2}{3}\frac{\mu m}{\mathrm{R}\nu}\left\{2\Sigma\left(\frac{\partial u_0}{\partial x}\right)^2 - \tfrac{2}{3}\left(\Sigma\frac{\partial u_0}{\partial x}\right)^2 - \Sigma\left(\frac{\partial v_0}{\partial z} + \frac{\partial w_0}{\partial y}\right)^2\right\}.$$

which is the equation of energy.

The Thermal Conductivity of a Gas.

§ 11 (C) In the equation of energy which we have just obtained, the second term on the right-hand side represents the change of heat per unit volume due to the variation in density at the point considered, while the third term may be proved equal to the heat produced by internal friction. The first term, by comparison with FOURIER's equation of conduction of heat (ϑ being the thermal conductivity and C_v the specific heat at constant volume), *i.e.*, with

$$\mathrm{C}_v\rho\frac{\partial \mathrm{T}}{\partial t} = \Sigma\frac{\partial}{\partial x}\left(\vartheta\frac{\partial \mathrm{T}}{\partial x}\right),$$

is seen to represent the change of heat by conduction, and to indicate that the coefficient of thermal conductivity of a gas is given by

$$(247)\qquad \vartheta = f\mu\mathrm{C}_v.$$

The value of f in this well-known formula is, for a general monatomic gas, given by (243), *i.e.*,

$$(248)\qquad f = \tfrac{5}{2}\sum_0^\infty\beta_r\Big/\sum_0^\infty\gamma_r.$$

In general f is a function of the temperature only.

Formulæ for μ and ϑ for Particular Molecular Models.

§ 11 (D) By substitution of the values of C_0 and $\Sigma\beta_r/\Sigma\gamma_r$ given in §§ 9, 10, for the particular molecular models there discussed, we obtain the following special cases of (237) and (248):—

(249) Rigid elastic spheres,

$$\mu = 1{\cdot}016\,\frac{5m}{64\pi^{1/2}\sigma^2}\left(\frac{\mathrm{R}}{m}\mathrm{T}\right)^{1/2} \qquad f = \tfrac{5}{2}\,.\,1{\cdot}010 = 2{\cdot}525,$$

(250) Attracting spheres,

$$\mu = (1+\epsilon_a)\frac{5m}{64\pi^{1/2}\sigma^2}\left(\frac{\mathrm{R}}{m}\mathrm{T}\right)^{1/2}\frac{1}{1+\mathrm{S}/\mathrm{T}} \qquad f = \tfrac{5}{2}(1+\delta_a),$$

(251) Centres of force r^{-n},

$$\mu = (1+\epsilon_c) \frac{75m}{8\pi^{1/2}{}_n\mathrm{A}_1\Gamma\left(4-\dfrac{2}{n-1}\right)}\left(\frac{\mathrm{R}}{m}\mathrm{T}\right)^{\frac{n+3}{2(n-1)}} \qquad f = \tfrac{5}{2}(1+\delta_c).$$

In these formulæ ϵ_a and ϵ_c denote the values of $\sum_0^\infty \gamma_r$ in the cases respectively when the molecules are attracting spheres and centres of force, and δ_a and δ_c similarly denote $\Sigma\beta_r/\Sigma\gamma_r$; their values are given in Tables V. and VI., and in no case differ from unity by more than two per cent.

The mode of variation of μ with the temperature affords a guide to the law of interaction between the molecules of actual gases. By comparison with experimental determinations of μ at various temperatures it is thus found that of the above models the one which most closely represents the behaviour of actual molecules in this respect, at ordinary temperatures, is the second, *i.e.*, a rigid elastic attracting sphere.*

Comparison of the present formulæ for μ and δ with those of my previous paper.

§ 11 (E) The general formulæ (237) and (248) for viscosity and thermal conductivity agree with those of my former paper,† except that the factors $\sum_0^\infty \beta_r$ and $\sum_0^\infty \beta_r/\sum_0^\infty \gamma_r$ were there omitted. This was in consequence of the assumption on which the analysis of that investigation was based, that F (U, V, W) is sufficiently represented by the terms of the first three degrees in U, V, W. We have seen in § 9 (C) that this is true for a gas composed of Maxwellian molecules, but not otherwise. It seems of interest to consider why the neglect of all the coefficients β_r, γ_r after $r = 0$ led to results of such accuracy; for the errors arising from the assumption are represented in the special cases (249)–(251) of (237) and (248) by the factors 1·016, 1·010, $1+\epsilon_a$, $1+\delta_a$, $1+\epsilon_c$, $1+\delta_c$, so that the necessary corrections to my previous formulæ do not exceed one or two per cent. ENSKOG, on the other hand, after deducing formulæ similar to (237), (248), but without evaluating the coefficients β_r, γ_r, made a first approximation by neglect of all these coefficients after $r = 0$, and arrived at the result $f = 5$ for rigid elastic spheres.‡ This was due to the fact that such a use of (237), (248), as they stand, involves not only the neglect of all the coefficients after $r = 0$, but also requires an assumption as to the values of β_0, γ_0 themselves, as, for instance, that they are approximately the same as for Maxwellian molecules; a comparison of (196) with Table IV. (p. 331) will show that this is far from being the case.

It may readily be seen, however, that the method of my former paper required no

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* At very low temperatures, however, the n^{th} power centre of force is the molecular model which gives by far the best representation of the relation between μ and T, in the case of helium; *cf.* KAMERLINGH ONNES and SOPHUS WEBER, 'Comm. Phys. Lab. Leyden,' 134B, p. 18, or JEANS' 'Dynamical Theory of Gases,' 2nd ed., §§ 405, 407.

† CHAPMAN, 'Phil. Trans.,' A, vol. 211, p. 433, *et seq.*

‡ ENSKOG, 'Phys. Zeit.,' XII., p. 58, 1911.

hypothesis as to the values of β_0, γ_0, which were determined from $\Delta \mathrm{UC}^2$ and $\Delta \mathrm{U}^2$ as in this paper; in effect, the later coefficients were neglected, while β_0 and γ_0 were obtained from the equations (138), (139) corresponding to $s = 0$. Viewed otherwise, my previous formulæ were equivalent to (237), (248) divided respectively by $\sum\limits_0^\infty \kappa_r\gamma_r/\kappa_0$ and $\sum\limits_0^\infty \kappa_r\beta_r/\sum\limits_0^\infty \kappa_r\gamma_r$. Thus the neglected factors in μ and f were

$$\frac{\sum\limits_0^\infty \kappa_0\gamma_r}{\sum\limits_0^\infty \kappa_r\gamma_r} \quad \text{and} \quad \frac{\sum\limits_0^\infty \beta_r}{\sum\limits_0^\infty \gamma_r} \cdot \frac{\sum\limits_0^\infty \kappa_r\gamma_r}{\sum\limits_0^\infty \kappa_r\beta_r},$$

which evidently reduce to unity if we neglect all the β'_0 and γ', after $r = 0$, without any assumption as to the values of β_0 and γ_0.

One of the main results of the former paper was that $f = \frac{5}{2}$ for all monatomic gases, and not only for those composed of Maxwellian molecules. This is now seen to require modification, but the values here found for f in the special cases which have been considered in §§ 9, 10 show that the correction needed to make the equation accurate is very small; it appears probable that for all likely molecular models f is very slightly greater than 2·5, and that it is nearly but not quite constant with change of temperature (except when the molecules are elastic spheres or centres of force proportional to r^{-n}).

Comparison of the Formulæ for μ and ϑ with the Results of other Theories.

§ 11 (F) The only kinetic theory of viscosity and thermal conductivity which could hitherto lay claim to numerical accuracy (within the limits imposed by the initial postulates) is MAXWELL's theory[*] of a gas composed of molecules of the kind dealt with in § 9 (C). The results of his theory are special cases of the general formulæ of this paper.

The theory of a gas composed of molecules which are point centres of force varying inversely as the n^{th} power of the distance had not been discussed in detail, previous to my own former paper. RAYLEIGH,[†] however, from considerations of dimensions alone, had deduced the law of variation of viscosity with temperature, and the same argument would also show that for such a gas f is an absolute constant (for any given value of n). Nothing was known as to the value of this constant, or of the numerical coefficient in the expression for μ, and it is a surprising result, which could hardly have been guessed *à priori*, that as n ranges from 5 to ∞ the value of f should vary only from 2·500 to 2·525 approximately.

The theory for molecules which are rigid elastic spheres exerting attractive forces was equally undeveloped. SUTHERLAND[‡] had taken an important step, however, in

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[*] MAXWELL, 'Collected Papers,' vol. II., p. 23.

[†] RAYLEIGH, 'Roy. Soc. Proc.,' vol. 6, p. 68, 1900.

[‡] SUTHERLAND, 'Phil. Mag.,' (5), 31, 1893.

deducing the correction to the law connecting μ and T (*i.e.*, $\mu \propto T^{1/2}$) for molecules which are rigid elastic spheres without attraction; he showed, without attempting numerical accuracy, but by a method which is correct in its main outlines, that the attractive forces necessitate an additional factor $(1+S/T)^{-1}$, as in (249). The law $\mu \propto T^{1/2}(1+S/T)^{-1}$ is more successful than any other in representing the observed relation between μ and T over a considerable range of temperature, and S is deservedly known as SUTHERLAND'S constant.

The theory of a gas composed of molecules which are rigid elastic spheres, which was taken by SUTHERLAND as the basis of his modified formulæ, has been developed along lines different from those of this paper by CLAUSIUS, MAXWELL, BOLTZMANN, MEYER, STEFAN, JEANS, and others. Their method was less analytical than the present one, and while it gave correctly the general relationships between μ, ϑ, p, ρ, and T, its results do not possess numerical precision. JEANS[*] notably improved certain of the formulæ due to earlier authors by taking into account the tendency of a molecule to persist, after a collision, in the general direction of its original course. For this reason his expression for the viscosity, viz.,

$$(252) \qquad \mu = \frac{0{\cdot}88}{4\pi}\,\frac{m}{\pi^{1/2}\sigma^2}\left(\frac{R}{m}T\right)^{1/2}, \qquad \text{(JEANS)}$$

approaches more nearly to the correct expression (249) than does the formula of any other author[†]. A comparison of (249) with (252) indicates that the latter is still too small by 12 per cent.; the error of the original formula, without JEANS' correction, was 30 per cent.

The numerical inaccuracy of the earlier prevailing theory of conductivity, which was due to MEYER[‡], was very great. Its result was generally given as

$$\vartheta = f\mu C_v \qquad \text{where} \qquad f = 1{\cdot}6027,$$

but Prof. L. V. KING, of McGill University, has pointed out to me by letter that MEYER'S argument really leads to the result

$$f = 1{\cdot}4161,$$

a numerical mistake having crept into his work which had not previously been detected. The correct value of f for rigid elastic spheres is given in (249), *i.e.*,

$$f = 2{\cdot}525.$$

This large error in MEYER'S theory indicates the difficulty of arriving at numerically accurate formulæ by the older "mean free path" method, and diminishes

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[*] *Cf.* JEANS' 'Dynamical Theory of Gases.'

[†] Apart from that in my former paper, which was 1·6 per cent. too small.

[‡] MEYER'S 'Kinetic Theory of Gases,' 2nd English edition, chap. IX.

confidence in other parts of that theory where detection of error is less easy. Until recently MEYER'S value of f received support from experimental data for diatomic gases, to which it does not really apply; only lately have data for monatomic gases been obtained, which, as we shall see, give values of f nearly equal to $\frac{5}{2}$.

§ 12. COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA.

The Variation of Viscosity with Pressure.

§ 12 (A) The main objects of a comparison of a mathematical theory with experimental data are either to test whether the postulates underlying the theory are valid, or whether the theory is itself mathematically correct. The present theory being exact, within certain defined limits, our purpose in this chapter is to consider how far the hypotheses underlying the analysis are well founded. The general validity of the foundations of the kinetic theory is attested in many ways, one of the most striking being the independence of viscosity and pressure in a gas. This law, when first discovered by MAXWELL, seemed so improbable that it gave a great stimulus to experimental research on gases, and the constancy of μ, when T is kept constant, has been verified over a range of pressure extending from a few millimetres of mercury up to more than one atmosphere. WARBURG and VON BABO have found that, in the case of carbon dioxide, the law begins to fail when the pressure becomes so great as 30 to 120 atmospheres, μ rising appreciably. In very rarefied gases, on the other hand, the viscosity falls *below* the value appropriate to the existing temperature. This must be referred to the failure of the postulates of our theory to represent the facts in these extreme cases, the molecules becoming too few for our statistical method to apply, on the one hand, while on the other our assumption that the molecular paths are rectilinear for the major part of the time, and our neglect of multiple encounters, become illegitimate.

The Variation of Viscosity with Temperature.[*]

§ 12 (B) Over a wide range of pressure and temperature, undoubtedly, the general postulates of our theory are true for actual gases. We cannot discover directly, however, the nature of the molecules or their mode of collision, and it is important, therefore, to examine which molecular model yields formulæ most in accordance with experimental data. For this purpose we naturally choose those properties which are most affected by the nature of the molecule; the chief of these is the variation of viscosity with temperature. MAXWELL abandoned his theory of a gas composed of rigid elastic spherical molecules because it led to the relation $\mu \propto T^{1/2}$, while his experiments gave the result $\mu \propto T$. This caused him to develop the theory of a Maxwellian gas (§ 9 (C)), for which $\mu \propto T$, but later experimenters have failed to confirm this law, and we must conclude that the molecules of actual gases behave during encounters neither like elastic spheres nor like Maxwellian molecules. The observed relation

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[*] The reader may be referred with advantage to the discussion of this point by JEANS in the second edition of his 'Dynamical Theory of Gases,' §§ 399–407.

between μ and T agrees much more closely with SUTHERLAND'S law $\mu \propto T^{1/2}(1+S/T)^{-1}$ than with any other; for example, SCHMITT* has found that the law is valid for hydrogen and helium from $-60°$ C. to 185° C., and BARUS has shown that it holds good for air over a wide range of temperature. The law has not been tested, for the former gases, above 185° C.

This seems to indicate that for the kinetic theory of gases at ordinary temperatures the best molecular model is an attracting sphere, and it is interesting to notice that this model is the one used by VAN DER WAALS with such success in deducing his famous law. Further confirmation is supplied by the excellent agreement between the values of the molecular diameters deduced on this hypothesis from the constant b of VAN DER WAALS' law and from the viscosity by means of my formula (250)—*cf.* § 12 (F).

At low temperatures SCHMITT*, BESTELMEYER†, VOGEL‡ and others have shown that the observed values of μ are greater than those predicted by SUTHERLAND'S law. This may be compared with the rise in the value of μ when the pressure is greatly increased, both effects probably having a like cause; in these states, when the mean free path of the molecule is much reduced, the molecular paths may cease to be approximately rectilinear between collisions, and multiple encounters will grow in importance. Since our theory rules out these contingencies, its results cease to be applicable, and a modification of the theory and its postulates is necessary if a proper account of these phenomena is to be given. In regard to this, one point which should be noticed is that in § 9 (E) a term $f_{2k}(y)$ in $\phi^{2k}(\tau y)$ was neglected (*cf.* (211)) which, if retained, would cause the law connecting μ and T to take the form

$$\mu \propto \frac{T^{1/2}}{1+(S/T)+f(T)}$$

where $f(T)$ can be expanded in the form $AT^{-2}+BT^{-3}+\ldots$. This term is due to the effect of the attractive forces in producing deflections without the occurrence of collisions, and is probably always small; but it may readily be seen that it is always positive, and that this correction would lead to a *diminution* in the theoretical value of μ at low temperatures. Clearly, therefore, the observed discrepancies cannot be attributed to our neglect of this small quantity.§

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* SCHMITT, 'Ann. d. Phys.,' 30, p. 399, 1909.

† BESTELMEYER, 'Munich dissertation,' 1903.

‡ VOGEL, 'Berlin dissertation,' 1914, where full references, and an interesting discussion of low temperature work on viscosity, are given.

§ VOGEL, in his dissertation, suggests as possible causes of the failure of the theory to represent the observed variation of μ with T at low temperatures (i.) a failure of the ordinary mechanics, such as is contemplated in PLANCK'S theory of quanta; (ii.) that the attracting sphere model no longer represents the molecule; (iii.) that $1+S/T$ should be replaced (according to my suggestion in 'Phil. Trans.,' A, vol. 211, p. 474, 1912) by $1+(S/T)\pm(C'/T)^2$. By the latter means a better accordance with observation is obtained, but the new term has the *minus* sign, and is therefore illegitimate.

The Thermal Conductivity of Monatomic Gases.

§ 12 (C) It is convenient to discuss the thermal conductivity of gases in terms of the constant f in the formula $\vartheta = f\mu C_v$, as this eliminates the necessity for a separate discussion of the dependence of ϑ on pressure and temperature; this is parallel with that of μ, and f is nearly or quite independent of pressure and temperature in normal conditions. As we have seen in § 11 (F), the value of f has been a matter of some uncertainty; so long as its value for rigid elastic spheres was supposed to be 1·6027, while for Maxwellian molecules it was known to be $\frac{5}{2}$, it seemed to offer a means of testing the suitability of different molecular models. On the ground of the discrepancy between the theoretical and observed relation between μ and T, Maxwellian molecules were known to be unsatisfactory representations of actual molecules. Until about 1900 no reliable determinations of f had been made for monatomic gases, and those found for diatomic gases agreed fairly well with MEYER's value of f (*i.e.*, 1·6027 or, more accurately, 1·416); at the time this was regarded as a confirmation of the rigid elastic spherical model of the molecule, and as indicating that the internal molecular energy, which is not taken into account in these theories of a monatomic gas, is transmitted at the same rate as the translational energy. When, in 1902, SCHWARZE obtained the values of f for argon and helium, and found them nearly equal to $\frac{5}{2}$, the conclusion to be drawn was not obvious. It certainly contradicted MEYER's theory, but left the question open as to whether the analysis, or the assumption of the rigid elastic spherical model, was at fault; also if $f = \frac{5}{2}$ indicated that the molecules are Maxwellian, the failure of the corresponding law connecting μ and T remained unexplained. It should be remembered, moreover, that the law $\mu \propto T^{1/2}$ for rigid elastic spherical molecules is equally contradictory to experiment.

These difficulties were removed by the theorem of my former paper, according to which f is an invariable constant $\frac{5}{2}$ for all monatomic molecules. This is now seen to be incorrect as a general theorem, but the deviations found for the various particular molecular models discussed leaves little room for doubt that f is very nearly equal to $\frac{5}{2}$ in the case of all likely models. The fact simply is, therefore, that f is very unsuitable as a means of discrimination between different models, and SCHWARZE's observations indicate some mathematical fallacy in MEYER's theory, without supporting any particular molecular model. The observed values of f are hardly known with sufficient accuracy to enable any conclusion to be drawn from a slight divergence from the value $\frac{5}{2}$, within the limits prescribed in (249) to (251). They are important, however, as confirming the general validity of the kinetic theory, apart from any hypothesis as to the nature of the molecules.

The following table contains all the available data concerning the value of f for monatomic gases. Only very recently has the conductivity of neon been determined, owing to the scarcity of the gas; for krypton and xenon its value is still unknown.

Table VII.—Values of f for Monatomic Gases.

Gas.	Absolute temperature. °C.	f.	Authority.
Helium	273	2·51	Schwarze[*]
		2·40	Eucken[†]
	81	2·23	Eucken
	21	2·02	Eucken
Argon	273	2·50	Schwarze
		2·49	Eucken
	91	2·57	Eucken
Neon	283	2·50	Dorn[‡]

These results for argon and neon and, to a less extent, for helium at normal temperatures agree very well with the theoretical value of f, especially since the combined experimental errors in their determination may easily exceed one per cent. at ordinary temperatures, and much more at low temperatures.

The diminution in the value of f for helium at low temperatures, if confirmed by further experiment, is very interesting and important. Helium is peculiar at low temperatures also in the striking divergence of its viscosity from Sutherland's law. Eucken suggests as the explanation of the former phenomenon a partial failure of interchange of molecular energy at collision, but (*cf.* Table VI. of his paper) down to 81° C., at any rate, the value of C_v for helium remains constant and appropriate to a gas which possesses only translational energy. A failure in interchange of translational energy would contradict the ordinary dynamical laws, and it is certainly desirable to seek some other explanation, if this be at all possible.

The alternatives are not numerous, and will be examined in turn. We may rule out a numerical error in the theory, of more than one per cent., as being quite improbable; but though all the molecular models discussed in this paper lead to values of f equal to or slightly greater than 2·5, it is conceivable that for some peculiar model f may have rather different values and a wider temperature range. I think this is unlikely, and that it is probably possible to prove that f always exceeds 2·5, but this is only a speculation; helium agrees so well at high temperatures, however, with Sutherland's law connecting μ and T, that its molecules can hardly be supposed so different in behaviour from rigid elastic attracting spheres as to make f theoretically equal to 2·0 at low temperatures.

Again, molecular aggregation might seem to afford an explanation, since if part of the gas were polyatomic through clustering of the molecules, the value of f would

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[*] Schwarze, 'Halle dissertation, Ann. d. Phys.,' (4), 11, p. 303, 1903.

[†] Eucken, 'Phys. Zeit.,' 14, p. 324, 1913, Tables 3, 6. Eucken (footnote 4 to p. 328) states that Schwarze's value of f for helium is too large owing to a miscalculation in determining C_v.

[‡] This result was kindly communicated to me by Prof. Dorn, of Halle, as an extract from 'Mitt. d. Naturf. Ges. z. Halle,' 4, 1914.

probably lie between 2·5 and the lower values characteristic of polyatomic gases. In this case, however, the value of C_v, the specific heat at constant volume, should rise to correspond with the internal energy of such molecules ; as the experiments indicate a constant value of C_v, the suggestion must be abandoned.

The only possible remaining hypothesis seems to be to attribute the fall in f to the neglect of multiple collisions between molecules, including also the effect of the attractive forces (in SUTHERLAND'S case) in producing deflections without collisions ; at low temperatures the molecules may be too close together for these postulates of our theory to continue valid. If we determine ϑ for helium from the formula $2{\cdot}5\mu\, C_v$, using the value of μ calculated from SUTHERLAND'S formula (which is less than the observed value at low temperatures, as we have seen), the result is less than that observed at low temperatures. Hence both ϑ and μ diminish with temperature less than is predicted by SUTHERLAND'S law, the divergence being greater for μ than for ϑ, so that f also diminishes. We cannot enter here into a test, by calculation, of this suggested hypothesis, but some confirmation might be sought experimentally by examining whether f is less than 2·5 for helium at normal temperatures but under considerably increased pressure. The latter would bring the molecules closer together in the same way as would a diminution of temperature, and this is all that our suggestion requires. It is known that over a large range of pressure μ and ϑ are constant, but that at high pressures μ increases ; the independence of ϑ on pressure has usually been tested by *diminishing* the normal pressures,* and experiments under increased pressure might throw valuable light on the present phenomenon. Gases other than helium may be expected to behave similarly, though perhaps only with lower temperatures or higher pressures.

§ 12 (D) The case of mercury vapour may also be mentioned, as it was the first monatomic gas for which f was determined. KOCH† determined μ for mercury vapour at 203° C., 273° C., and 380° C., while SCHLEIERMACHER‡ determined ϑ at 203° C. These data, together with the theoretically calculated value of C_v, led to $f = 3{\cdot}15$. MEYER and others have raised objections to the determinations of μ (*a*) because the three values show an improbable amount of variation with temperature, and (*b*) because of the vitiating effect of condensed mercury on the walls of the capillary tube used in the experiments. VOGEL§ has made a re-calculation of μ for mercury from an interesting formula which he gives, and finds that at 573° C. absolute|| μ should equal $593{\cdot}10^{-7}$; this, combined with SCHLEIERMACHER'S result, reduces f to 2·80. But it is desirable that more accurate experiments should be made in order that a thoroughly reliable value of f may be obtained.

---

* EUCKEN, 'Phys. Zeit.,' 12, p. 1103, 1911, Table 2.

† KOCH, 'Wied. Ann.,' 19, p. 857 (1883).

‡ SCHLEIERMACHER, 'Wied. Ann.,' 36, p. 346 (1889).

§ VOGEL, 'Berlin dissertation,' p. 57, 1914.

|| So given by VOGEL ; it may be a misprint for 473° C.

The Thermal Conductivity of Polyatomic Gases at Low Temperatures.

§ 12 (E) The formula $\vartheta = f\mu\,C_v$ is true for polyatomic as well as for monatomic gases, f being independent of pressure and temperature over a considerable range. Under normal conditions, however, its value is 2·0 or less, being greatest for diatomic gases and diminishing down to about 1·5 for complex molecules. EUCKEN* has made the interesting and important discovery, however, that diatomic gases show an increase in f at low temperatures, the conductivity varying with temperature in the sense opposite to that observed in the case of helium. This is apparent, to a slight extent, in nitrogen, but is most striking in the case of hydrogen. It is found that, simultaneously with the rise in f, the specific heat C_v progressively falls in value until at 21° C. absolute its amount is that appropriate to a monatomic gas of the same molecular weight. At these low temperatures the rotatory motion of the molecules seems to fail, for some reason as yet undiscovered, so that the gas behaves in certain respects as if its molecules were of the spherically symmetrical type discussed in this paper. It is highly interesting and significant that this approach to monatomicity is accompanied by an upward tendency of f towards the value (2·5 approximately) which is appropriate to monatomic gases. The same phenomenon may be expected in the case of the other diatomic gases, at lower temperatures corresponding to their lower boiling points. In the following table* the results for hydrogen alone are given; the number n in the third column represents the number of "degrees of freedom" of the molecule, as calculated from the observed values of C_v.

VALUES for f for Hydrogen.

Absolute temperature.	f.	n.
° C.		
273	1·96	4·80
195	2·09	4·41
81	2·25	3·16
21	2·37	2·98

The Diameter of the Molecule.

§ 12 (F) In my former paper tables were given showing the values of the molecular diameters for several gases, calculated on the hypothesis that the molecules are rigid spheres, with or without attractive force. These require a small correction to be strictly accurate, on account of the factor $(\Sigma\gamma_r)^{1/2}$ there omitted from the formula for

---

* *Cf.* EUCKEN, 'Phys. Zeit.,' 14, p. 329, 1913, Table 6.

σ in terms of μ. In this paper I shall give only a few values of σ, calculated from recent data and from the exact formula

$$\sigma^2 = (1+\epsilon_a)\,\frac{5m}{64\pi^{1/2}\mu\,(1+\mathrm{S}/\mathrm{T})}\left(\frac{\mathrm{R}}{m}\mathrm{T}\right)^{1/2}$$

$$= \frac{0{\cdot}491\,(1+\epsilon_a)\rho\,\overline{\mathrm{C}}}{2^{1/2}\pi\nu\mu\,(1+\mathrm{S}/\mathrm{T})}$$

appropriate to attracting spherical molecules. The values of S are determined from the variation of viscosity with temperature, $\overline{\mathrm{C}}$ is the mean molecular velocity, while ϵ_a is found from Table VI. (in all the cases here considered it is quite negligible).

In the following table values of the diameters calculated from the constant b of VAN DER WAALS' law are also given for comparison. The agreement between the two sets of values is in most cases remarkable, and the table as a whole is a testimony to the close numerical accuracy now attained by the kinetic theory; where there is disagreement in the table there is in most cases uncertainty as to the data.

While exact agreement may be expected only for monatomic gases, the values for diatomic gases show that our theory gives a mean diameter, in other cases, which agrees with that found for b; the internal energy which prevents the application of our formulæ to the conductivity of polyatomic gases hardly affects viscosity.

TABLE VIII.—Molecular Diameters Calculated from Viscosity and VAN DER WAALS' Law.

Gas.	$\mu_0\cdot 10^7$.	S.	$1+\epsilon_a$. (Table V.)	VAN DER WAALS' b.	$2\sigma_1\cdot 10^8$ (viscosity).	$2\sigma_2\cdot 10^8$ (VAN DER WAALS.)
Argon	2107	162	1·002	0·001347	2·84	2·85
Krypton	2334	182	1·001	0·001774	3·12	3·14
Xenon	2107	252	1·000	0·002304	3·47	3·42
Helium	1885	75	1·006	0·000432	1·89	1·96
Oxygen	1923	130	1·005	—	2·93	2·89
Hydrogen	854	76	1·006	0·00096	2·36	[2·52]
Nitrogen	1672	112	1·003	0·00255	3·10	3·54 3·08
Air	1721	111	1·004	0·00209	3·08	3·30
Carbon dioxide . .	1388	249	1·000	0·00228	3·27 3·20	3·40 3·20

REFERENCES.

Viscosity μ_0 at 273° C. absolute.—These values are taken from the table on p. 476 of my first memoir, where full references may be found. They agree very well with the list given by EUCKEN ('Phys. Zeitschr.,' 14, Table 3, 1913), in which VOGEL's determinations are included with other recent values in taking means.

SUTHERLAND'S *constant* S.—These values are those given in the same table of my former memoir (what is called S in this paper was there, and is usually, denoted by C), where references to sources may be found. The value for krypton was there given incorrectly; I am indebted to Dr. G. RUDORF for the correction.

VAN DER WAALS' *b*.—The values for helium (KAMERLINGH ONNES), hydrogen, nitrogen, air (ROSE-INNES), and carbon-dioxide (VAN DER WAALS') are taken from JEANS' 'Dynamical Theory of Gases,' 2nd edition, § 194. Those for argon, krypton, and xenon (RAMSAY and TRAVERS), from RUDORF, 'Phil. Mag.,' June, 1909, p. 795, are not direct experimental values, however, but are calculated from critical data.

Diameter $2\sigma_1$ *from viscosity.*—These are practically twice the values for the radii given on pp. 476, 481 of my former memoir, where, however, errors of calculation (here corrected) were made in the case of argon and krypton (as Dr. G. RUDORF kindly indicated to me).

Diameter $2\sigma_2$ *from* VAN DER WAALS' *b*.—The value for oxygen, and the second values for nitrogen and carbon-dioxide (as well as $2\sigma_1$ for the latter) are from Table 7 of EUCKEN'S paper; he does not give his authorities, but his values are probably the most recent and reliable. The value for hydrogen, he says, is doubtful.

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VII. *The Newtonian Constant of Gravitation as Affected by Temperature.*

By P. E. SHAW, *B.A., D.Sc.*

Communicated by C. V. BOYS, *F.R.S.*

Received October 19,—Read December 2, 1915.

CONTENTS.

I. INTRODUCTION.

1. THIS paper deals with the possible existence of a temperature coefficient in the law of gravitation and gives an account of experiments made to discover this coefficient. The apparatus used is of the Cavendish torsion-balance type, and the range of temperatures is from 15° C. to 250° C. The result of a prolonged research is shown in the summary.

The accumulation of negative results in the experimental study of gravitation is remarkable. In consequence of the indifference of the gravitative force to changes of conditions (other than those given by the simple law $f = \mathrm{G}Mm/d^2$), none of the many theories of gravitation so far propounded has received general acceptance for lack of data wherewith to test them. Some recent theories, which consider the possibility of temperature effect, are :—

N. MOROZOV[*] advances a wave theory on which the attraction of masses would vary with temperature.

G. MIE,[†] a theory of matter which includes among its corollaries a temperature coefficient of $1/10^{13}$ per 1° C. to the "so-called Newtonian constant."

N. BOHR,[‡] in a paper on the constitution of the atom, assumes that gravitation like radio-activity is unaffected by all physical and chemical agencies, and hence the writer ascribes both these properties of the atom to its nucleus; whereas other physical properties are due to the electrons in the outer regions of the atom. But it should be noted that, at least as regards temperature, the data for gravitation are deficient. It is not easy to conduct experiments on a short range of one or two hundred degrees (see later) which is a small portion of the thousands of degrees of known measured temperatures. So it is necessary to speak with diffidence on this special branch of the subject of the constitution of the atom.

2. Determinations of the Newtonian constant have hitherto been made at ordinary temperatures only, special care being taken to maintain uniformity in temperature throughout the apparatus used; otherwise convection in the air or strains in the movable system might produce grave errors. This is shown repeatedly in the well-known researches by Prof. C. V. BOYS[§] and Prof. J. H. POYNTING.[‖] The necessity of providing a steady temperature about the delicate parts of the apparatus has hitherto been considered an insuperable bar to any direct experiment to discover a temperature effect for G. In fact, in 1905, shortly before the present research began, the late Prof. POYNTING and Mr. P. PHILLIPS[¶] wrote as follows:—"The difficulties of exact determination (of the Newtonian constant) at ordinary temperatures are not yet overcome and at very high or low temperatures they would be so much increased that the research seems at present hopeless."

3. Yet indirect investigations have been made. POYNTING and PHILLIPS[**] counterpoised a mass of 208 gr. on a balance and varied its temperature between 100° C. and −186° C. They came to the conclusion that the resulting change in weight, if any, is less than $1/10^9$ for 1° C. for the range 100° C. to 0° C. and $1/10^{10}$ for 1° C., for the range 0° C. to −186° C.

Another balance experiment on change in weight with temperature by SOUTHERNS[††] led to a somewhat similar result.

---

[*] 'Jurn. Russik Chimičisk Obščestva,' 40, 2, pp. 23 to 35, 1908.

[†] 'Ann. der Phys.,' 1913, No. 1.

[‡] 'Phil. Mag.,' July 26, 1913.

[§] 'Phil. Trans.,' 1895.

[‖] 'Phil. Trans.,' 1891.

[¶] See 'Roy. Soc. Proc.,' A, vol. 76, p. 445, 1905.

[**] *Loc. cit.*

[††] 'Roy. Soc. Proc.,' A, vol. 78, 1906.

4. In looking for a method to continue and extend these researches it should be observed that a weight of, say, 1 gr. can be determined by a first-rate balance to $1/10^8$, under favourable conditions,* whereas in a gravitation apparatus (*e.g.* that of C. V. Boys) the attraction of one mass to another cannot be found to be better than $1/10^5$ at the utmost. Thus, apart from other reasons, it would be futile on the latter type of apparatus to look for a temperature effect (at least between 100° C. and −186° C.) on the small mass m, since the above negative results have established the result with the greatest possible accuracy.

But in these balance experiments of Poynting and Phillips the large mass M (in this case the earth) is unchanged in temperature. Now M is incomparably larger than m and may have a preponderating influence, whereby change of *its temperature alone* would affect the mutual attraction. In the paper quoted Poynting and Phillips suggested (though without any *a priori* grounds) the feasibility of some such expression as the following :—

$$f = \mathrm{G}\left[1 + \kappa\frac{(\mathrm{M}t + mt')}{\mathrm{M}+m}\right]\frac{\mathrm{M}m}{d^2}, \quad \ldots\ldots\ldots \quad \mathrm{I.}$$

where κ is a temperature coefficient and t, t' are increments in temperature of M and m.

When M/m is very great, this reduces to

$$f = \mathrm{G}\,[1 + \kappa t]\,\frac{\mathrm{M}m}{d^2}, \quad \ldots\ldots\ldots \quad \mathrm{II.}$$

so that, on the above supposition, the mutual attraction would be influenced by change in temperature of the large mass only.

Admitting the possibility involved in II., we must abandon weight experiments, and proceed to the use of a full gravitation apparatus, having both masses (M and m) under control as regards temperature.

It is supposed by some that Kepler's 3rd law establishes the constancy of G, but I have tried to show† that this is false, and that the common practice of obtaining the masses and densities of heavenly bodies (sun, earth, planets, &c.) by assuming the invariability of G is at fault.

5. The above appears to me one case in which Kepler's laws have been strained beyond their legitimate use; another case was pointed out long ago by M. Vicaire.‡ He showed that when one of two attracting gravitative masses, M, is very large compared with the other, m, the fact that the acceleration of the latter is independent of its mass follows in all cases where the law of attraction is of the form

$$\mathrm{M}^k f\left(\frac{m}{\mathrm{M}}\right)\frac{1}{d^2}$$

---

* See Poynting's paper, 'Phil. Trans.,' 1891.

† See 'Nature,' 7 Oct., 1915.

‡ 'Comptes Rendus,' vol. 78, pp. 790 to 794.

k being any number and f any function expansible by TAYLOR'S theorem which vanishes with m/M. For on expanding by MACLAURIN'S theorem we have

$$\text{acceleration} = \mathrm{M}^{k-1}f'(0)\,\frac{1}{d^2}.$$

This is independent of m and therefore satisfies the experimental facts. There is an application of VICAIRE'S principle to the present subject; for k might vary according to the temperature of the large attracting body. It need only be constant as long as all the physical conditions (other than mass) are constant.

II. INDIRECT EXPERIMENTAL EVIDENCE.

1. It was pointed out by POYNTING and PHILLIPS (see paper quoted) that as regards small changes in temperature near, say, 15° C., there can be no great variation in weight with temperature as shown from various common experiments of great precision: (1) pendulum experiments give an appreciably constant value of gravity (g) regardless of the small temperature differences occurring at different times; (2) the value found for the expansibility of a liquid, say, mercury, is appreciably the same whether the dilatometer method or weight thermometer method be used. But the temperature range is very small, and we must not conclude from this or from the experiments of POYNTING and PHILLIPS on weight, that there would be no temperature influence on weight if the range of temperature were great.

2. A survey of previous researches on gravitation affords some slight information as to temperature effect:—

(1) The temperature of mountain masses and of superficial shells of the earth's surface to a depth of, say, half-a-mile, is well above ordinary laboratory temperatures. Hence values of G or of earth's mean density, Δ, obtained by these "earth" methods might differ from those obtained by laboratory methods. The most accurate earth methods, say those of MENDENHALL, PRESTON, VON STERNECK, give a rounded average for Δ of 5·4 c.g.s., whereas the best laboratory methods, say, by BOYS, BRAUN, POYNTING, RICHARZ, and KRIGAR-MENZEL, give a mean of 5·51. As the numbers stand they show a *plus* temperature coefficient for G (for G varies inversely as Δ). But inasmuch as the differences between the various "earth" results are much greater than between the numbers 5·4 and 5·51, no sure inference can be drawn.

(2) It has been pointed out by Prof. W. M. HICKS that BAILY'S results for Δ show a fall in value as temperature rises. This again indicates a *plus* temperature coefficient for G.

(3) From CORNU'S researches* the mean value of Δ from winter work was 5·50, from summer work 5·56. But in the absence of recorded temperatures we can deduce nothing. The apparatus in a laboratory may have a higher temperature in winter than in summer.

---

* 'Comptes Rendus,' vols. 76 and 86.

(4) Prof. C. V. **Boys** kindly gave me access to the note-books compiled by him in his research on Δ at the Clarendon Laboratory. I found there six complete experiments in which temperature was systematically recorded. Giving all the experiments equal weight, we find three whose value for Δ is below 5·52, the average being 5·517, and mean temperature 15°·9 C.; while the other four which have Δ above 5·52 average 5·528, with mean temperature 13°·8 C. This would show a *plus* temperature coefficient for G of 1/500 for 2° C. rise in temperature. In fig. 1 a graph is shown of these results.

(5) **Von Sterneck*** showed that the temperature gradient at a given depth in a mine varies from one mine to another, and that the mean density Δ for the whole earth, deduced from his pendulum experiments in the mines, increases as gradient increases. This again indicates a *plus* temperature coefficient. When the pendulum is swinging in a mine the strata immediately above and below would have an influence on the pendulum period out of proportion to their masses, on account of their proximity to the pendulum, consequently their temperatures would influence the results for Δ, supposing the existence of a temperature effect. Let us suppose a *plus* temperature coefficient. The strata below would always be at higher temperature than those above and would attract more strongly than the latter. In the case of high gradient this difference in attraction would be greater than when the gradient is low, and the result of the experiments would be an apparent value of Δ greater for high gradients than for low.

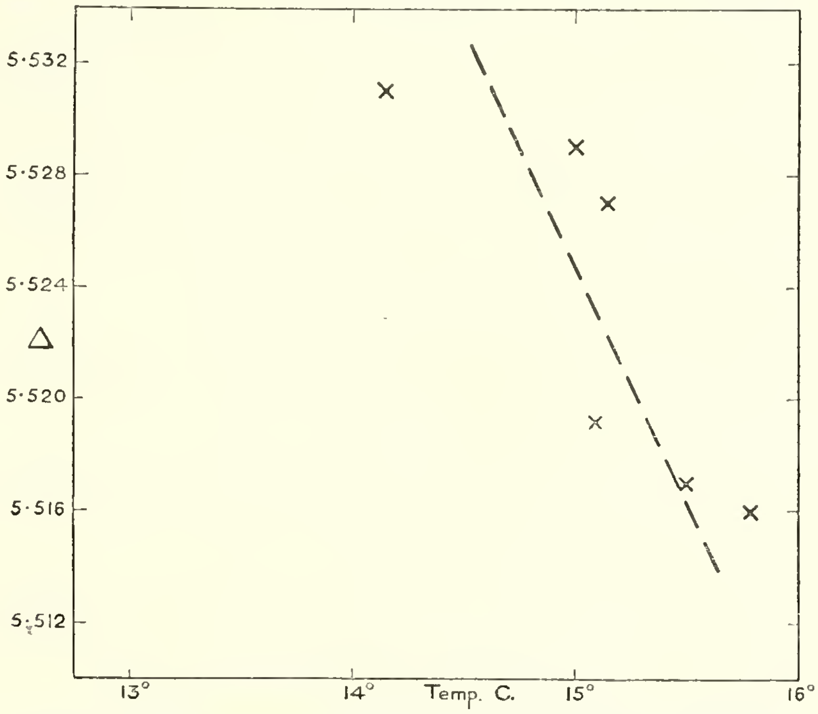

Fig. 1. Shows the relation Δ/θ in C. V. Boys' experiments.

3. Of the five sources of evidence above, one is useless from uncertainty as to temperature; but in the other four, in all of which the direction of temperature difference is known, an apparent *plus* temperature coefficient for G is found. There

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* 'Akad. Wiss. Wien.,' 1899.

is only a 1/16 chance that this accordance is mere coincidence. Yet the evidence is slender in view of the uncertainties of such delicate measurements which may involve spurious effects of this order of magnitude.

In the case of the results in BOYS' research we have data quite definite, though small, as to temperature, and they are outside the range of experimental error. On the whole we are led to expect that in a *full* gravitative experiment where both M and m are involved we should find a *plus* temperature coefficient of the order 1/1000 for 1° C.

After §§ 3 to 5 (pp. 350 and 351) we see that this result need not be at variance with the numerical figures obtained by POYNTING and PHILLIPS.

In this subject there are three classes of work, the results from which should at present be kept separate, viz. :—(1) Change in temperature of both M and m (*indirectly* by BOYS, BAILY, VON STERNECK and other pit experiments) ; (2) change in temperature of M only (*directly* by the present research, *indirectly* by MENDENHALL) ; (3) change in temperature of m only (*directly* by POYNTING and PHILLIPS).

There is only one class of experiment with which the present experiments can be brought into direct comparison, viz., the Schehallien type, and for this class we have no assigned temperatures.

III. METHODS EMPLOYED.

1. There are left two possible lines of research with a full gravitative apparatus on the influence of temperature on attraction.

(1) Changing temperature for M and m and the intervening medium ; (2) changing temperature of M alone.

I commenced with method (1), but abandoned it after much labour, the difficulties appearing insuperable. A decisive result obtained for the method (2) should go far to settle the whole issue *for the temperature range* involved.

As to the actual type of apparatus used there are three standard forms (*a*) the torsion balance ; (*b*) the weight balance ; (*c*) the pendulum.

The torsion balance was chosen as combining great sensitiveness with accuracy. Under favourable conditions the results agree by this method to 1/10,000 so that it affords unparalleled refinement ; but there are two great troubles attending this extreme delicacy, viz. :—

(1) The law, for maximum load on the fibre short of breaking, is

$$\text{sensitiveness} \propto 1/(\text{diam. of fibre})^2,$$

since carrying power varies as $(\text{diam.})^2$, and stiffness to torsion varies as $1/(\text{diam.})^4$. Thus for attainment of the best results one employs a small factor of safety in loading the fibre and breakages easily occur. Quartz fibres (as used chiefly here) often stand a load for many hours and then break. Hence all fibres before use must be subjected to careful load-time tests. Even after taking this trouble a small shock during installation may cause breakage.

(2) Trouble attends the use, as in these experiments, of a vacuum. The beam of a torsion balance has five degrees of freedom, and each mass suspended from the beam end has two effective degrees of freedom. In a vacuum, where damping is small, the beam system often gets beyond control.

To come to details, the large attracting masses outside the vacuum will be denoted as before by letters M, M, and the small ones inside the vacuum by letters *m*, *m*. The masses used are of various forms: (*a*) spheres; (*b*) cylinders, with axes vertical; (*c*) the approximately cylindrical form of vertical chains. The spherical form is the most sensitive, yet the cylinder has two advantages. It is compact for some heating purposes; also the law of force for cylinders involves distance to the first power approximately, so that error in position is not so serious as for spheres where the square of distance is involved. The law for spheres being well known, that for cylinders only will be proved :—

2. *The Law for Cylinders.*—The law of force for infinite parallel cylinders, one having much greater sectional area than the other, is found thus :—

Let the small cylinder cut the paper normally at O. Its attraction on unit mass at P = $2Gm_1/R$, where R = distance from P normal to the cylinder, and m_1 = mass of unit length of the cylinder. Let the second parallel cylinder of large section have axis at O′ and have mass per unit length m_2. Consider element of cross-section *ds* at P. Its mass $= \dfrac{m_2\, ds}{\pi a^2}$, where a = radius of cylinder.

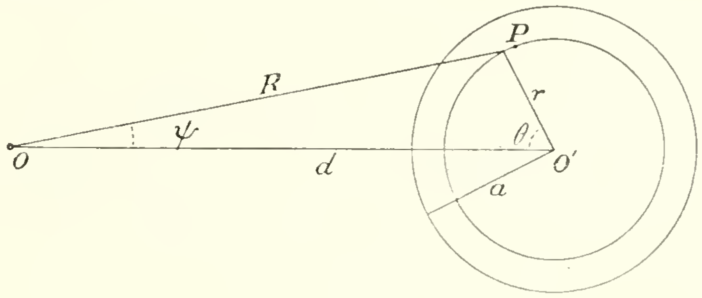


Fig. 2.

The total attraction per unit length is

$$F = \frac{2Gm_1m_2}{\pi a^2}\iint\frac{\cos\psi\,.\,ds}{R},$$

the integral to be taken over the whole cross-section of the cylinder. Using the symbols in the figure

$$R\cos\psi = d - r\cos\theta$$

$$R^2 = d^2 + r^2 - 2d\,.\,r\cos\theta$$

$$ds = r\,.\,dr\,.\,d\theta,$$

therefore

$$\frac{\cos\psi\,.\,ds}{\mathrm{R}} = \frac{(d-r\cos\theta)\;r\,.\,dr\,d\theta}{d^2+r^2-2d\,.\,r\cos\theta}$$

$$= \frac{1}{2d}\left(\frac{d^2-r^2}{d^2+r^2-2d\,.\,r\cos\theta}+1\right)r\,.\,dr\,.\,d\theta,$$

therefore

$$\mathrm{F} = 2\,\frac{2\mathrm{G}m_1m_2}{a^2}\int_o^a \frac{r\,dr}{d}$$

$$= 2\mathrm{G}m_1m_2/d \quad \ldots\ldots\ldots \quad \mathrm{I.}$$

for finite cylinders (M and m) whose length (l) is great *cf.* with the distance between the axes, we have approximately

$$\mathrm{F} = 2\mathrm{G}\,\frac{\mathrm{M}}{l}\cdot\frac{m}{l}\cdot l/d$$

$$= 2\mathrm{GM}m/ld \quad \ldots\ldots\ldots \quad \mathrm{II.}$$

hence increase in length of the cylinder, for constant mass, decreases sensitiveness, since l increases faster than d decreases.

The exact solution for finite cylinders would be exceedingly difficult and for present purposes is not required.

3. *The Sensitiveness Attainable for Spherical Masses.*—Many factors are involved. Let a = arm of the torsion balance, n = rigidity of fibre, r and l equal respectively radius and length of fibre, θ = angular twist of fibre ($\propto$ sensitiveness), K = moment of inertia, and T = period of the torsion system. Using other letters as before, we have

$$\text{couple} = \frac{2\mathrm{GM}ma}{d^2} = \frac{\pi n r^4\theta}{2l},$$

therefore

$$\theta = \frac{4\mathrm{GM}ma}{d^2}\cdot\frac{l}{\pi n r^4}\,; \quad \ldots\ldots\ldots \quad \mathrm{I.}$$

but $\mathrm{T}^2 = 8\pi^2\mathrm{K}\dfrac{l}{\pi n r^4}$, therefore

$$\theta = \frac{4\mathrm{GM}ma\mathrm{T}^2}{d^2\,.\,8\pi^2\mathrm{K}} \quad \ldots\ldots\ldots \quad \mathrm{II.}$$

When M, m are close together, m being small, we have

$$\mathrm{M} \bumpeq \tfrac{1}{6}\pi\,d^3$$

therefore

$$\theta = \frac{4\mathrm{GM}ma\mathrm{T}^2}{(6\mathrm{M}/\pi)^{2/3}\,.\,8\pi^2\mathrm{K}} = \frac{\mathrm{CM}^{1/3}ma\mathrm{T}^2}{\mathrm{K}}$$

where

$$\mathrm{C} = \text{constant},$$

but $\mathrm{K} \bumpeq ma^2$, therefore

$$\theta = \mathrm{CM}^{1/3}\,\mathrm{T}^2/a. \quad \ldots\ldots\ldots \quad \mathrm{III.}$$

This is the point established by C. V. Boys that for a given convenient value of T, θ varies as $1/a$ and is independent of m. Hence we make the beam short for sensitiveness. As to the value of T, we find the system is easily worked if the period does not exceed 5 mins.; but when it approaches 30 mins., the control is insufficient. It is well to aim at a value of T about 4 mins.

In my experience the best quartz fibres are of about 15μ diam. Taking this as the size of the fibre and knowing its length we arrive at m. Hence for a given value of T we obtain the length of the beam. Equation III shows that sensitiveness $\propto M^{1/3} \propto RD^{1/3}$, where R, D are the radius and density of the large sphere.

We see, then, that radius rather than density of M should be large. Thus copper would do almost as well as lead, provided it can be obtained equally free from magnetic impurities. I used lead, partly for its greater effect, partly for purity, and partly for economy, but for high temperature work where lead would melt, copper or other material of high melting point would be used.

IV. Precautions.

1. Apart from gas effects, there are two kinds of force to be avoided, viz. :—

(*a*) *Electrostatic.*—Entirely surrounding the vacuum vessel, except at the window, are metal tubes through which tap water flows. This system forms a perfect earthed screen between any external field and the movable system. But it is possible that in a vacuum charges may arise on gas particles leaving the solid surfaces after occlusion; or some internal charge may arise in some other way. Any such charge should be removed by the "earthed" metal lining to the vacuum vessel.

Again, charges arising from contact of different metals were avoided by having all the materials composing the beam system (including the lining sheath of the tube mentioned above) made of the *same* metal. Thus, in the final arrangement, the balls, m, m, the wires carrying them, the beam frame, and the mirror case were of the purest silver. The only foreign materials in the whole system were the small beam mirror and a minute amount of Margot's solder (see p. 364) used to fix the mirror case to the beam wire.

(*b*) *Magnetic.*—Impurities of iron, nickel and cobalt were avoided in the materials composing M, m and all parts connected to them. After working any of these with a tool, or after handling, the surfaces were dipped in nitric acid and well washed.

Iron screws, clamps, &c., were not used on parts of the apparatus adjoining M, m. If the internal, moving, system were entirely unmagnetic then magnetism of the outer parts would not matter; but suppose the inner system is slightly magnetic, it would respond to any magnetic influence, say, from M. When temperature is changed this response would change also, for the permeability of M would change with temperature. Thus we should have an apparent change in gravitative attraction, and this spurious effect would be hard to disentangle from the true gravitative temperature effect as they would both be cyclical.

2. We now come to the action of the gas remanent in the vacuum tube. The mechanical effects which this produces on the delicate torsion system are very complex. There are four distinct influences at work, viz., convection, radiometric pressure, discharge of occluded gases, damping :—

(*a*) *Convection.*—This causes great trouble in the ordinary gravitation experiments ; here, where temperature is greatly changed, it would make measurements at normal pressures useless. Hence we use a vacuum. In the highest attainable vacuum, convection would quite vanish. We even find that for a poor vacuum of about 1 mm. it produces little disturbance in a properly screened apparatus.

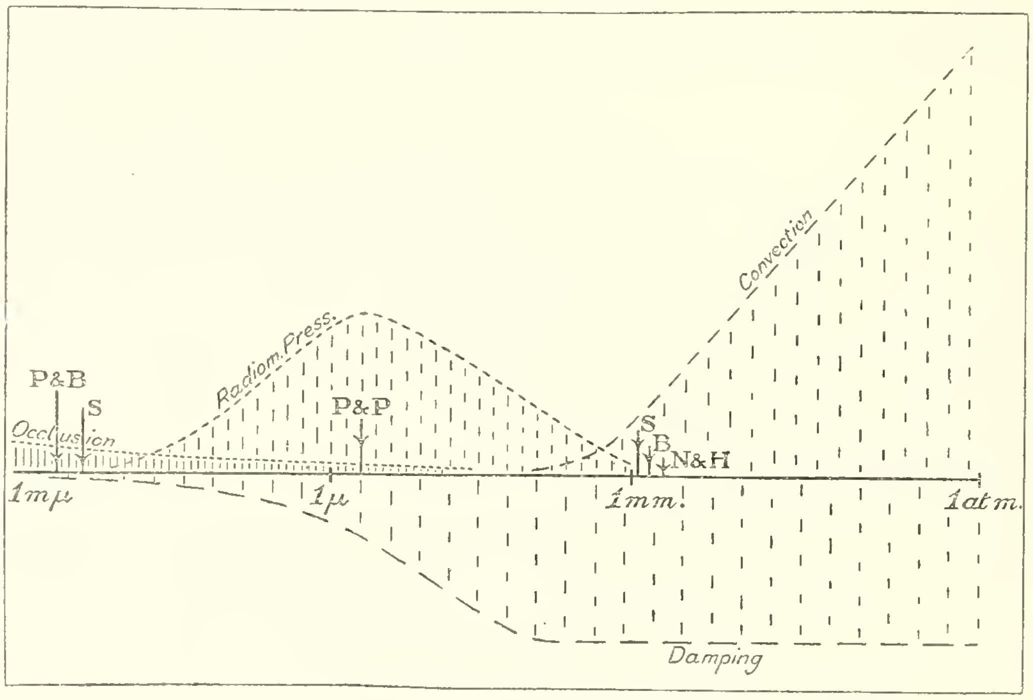


Fig. 3. Gas troubles depending on pressure in a vacuum.

(*b*) *Radiometric pressure* is a maximum at a pressure of 30μ of mercury ($\mu = 1/1000$ mm.). It has been detected at a pressure of $0{\cdot}015\mu$, but it is negligible for lower pressures and probably for pressure higher than 1 mm. with due precautions.

(*c*) The evolution of *occluded gas* from the wall of the vacuum vessel and from the torsion system should be negligible, even in a high vacuum, after long continued exhaustion with heat, as in these experiments.

(*d*) In a high vacuum the *damping* of the torsion system of great period is perceptible, though slight. But it is essential that the tremors continually received by the torsion system from the ground should be *quickly* damped out if accurate telescope readings are to be taken. The present research has been carried out in the heart of Nottingham, with a trunk railway system a quarter of a mile away, so that even in the dead of night it has been impossible to use high vacuum, except for the particular case when m, m have the form of chains. But a low vacuum of 1 mm., or greater, acts well, especially with the work performed between 9 to 5 at night.

It is important to attain the best conditions in the action of all these gas factors (which appear to be mutually incompatible).

The accompanying graph shows gas pressure as abscissæ on a logarithmic scale, while the ordinates indicate trouble due to any factor at any pressure.

The proportions are conjectural, depending on the conditions of any particular experiment. Convection is roughly proportional to pressure down to a vanishing quantity below 1 mm. Damping, unlike convection, is nearly independent of pressure to about 100μ. It is represented below the axis of abscissæ as being a blessing rather than an evil in these experiments. I have worked in these experiments chiefly at about 14 mm. and about $20m\mu$ (*i.e.*, 20×10^{-6} mm.). It will be seen that these two are favourable regions. Poynting and Barlow (P. and B.) used a very high vacuum in their research on recoil from light. Braun (B.) in the determination of the Newtonian constant had pressure of 4 mm., while Nichols and Hall (N. and H.) worked at 16 mm. in their research on radiation pressure.

As distinct from the above we have Poynting and Phillips (P. and P.) working in their weight experiments at 16μ which is unfavourable, as being in the thick of the radiometer region, and although convection which they specially feared would at that pressure be negligible deocclusion for the temperature 100° C. might be considerable.

3. *Radiation Pressure.*—This is yet another factor which must be borne in mind. The practice is to maintain the lamp for illuminating the telescope scale steadily alight before and throughout the experiment and to keep it practically constant in position. No other lamp comes within view of the interior of the apparatus. Moreover, for the elimination of this and of the gas actions, the walls of the vacuum are maintained uniform in temperature. Taking these precautions it is expected that the radiation pressure on the mirror of the suspended system will be constant throughout and will thus introduce no error.

Besides the many precautions mentioned, there are others incidental to the use rather than the design of the apparatus and will therefore appear in the detailed account following.

V. Early Experiments.

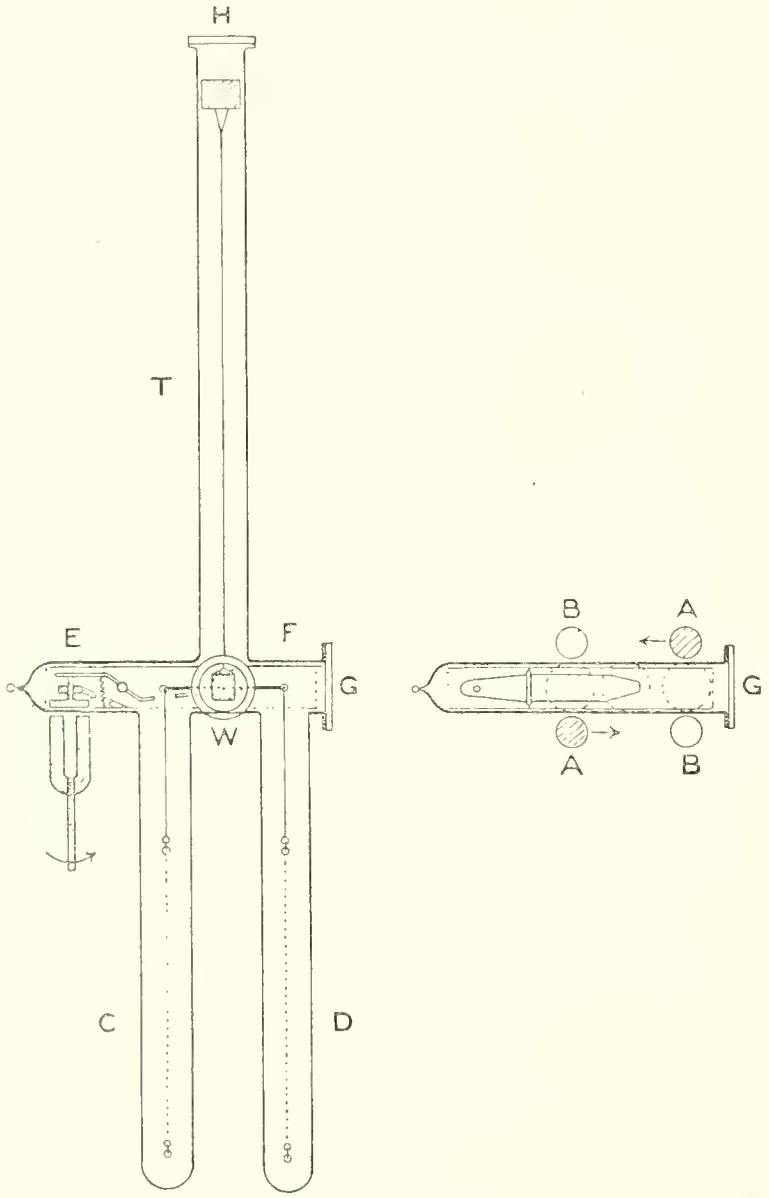
The Cavendish experiment has been developed to high excellence, but there is no previous investigation on the temperature effect to indicate the best way to avoid the many troubles sure to beset the investigation. The early methods, briefly mentioned below, failed for reasons given in each case, but they provided useful experience :—

(1) The first apparatus used was made of brass of special purity. The large masses were rods of lead coated with gold and the small ones were of purest gold wire. These were all hung together in the brass vacuum vessel. This form was

abandoned on account of the difficulty of maintaining a high vacuum in a metal vessel.

(2) Next I tried, as the vacuum case, a glass tube 160 cm. long, 2·5 cm. bore. The small masses were wires, and the large ones, now outside the vessel, were also stout wires. This particular form of suspension, if in high vacuum, retains any vibrations it may receive with great persistency, so the apparatus was set aside.

(3) The third form was a glass vessel provided with a window, W, and two other flanged openings, G, H (see elevation fig. 4, and plan section fig. 5). It was very sensitive; in one experiment the period was 33 mins., and the scale movement was 560 mm. The beam is shown carrying the small masses, m, m in chain form. The whole suspended system was of purest aluminium. The large masses, M, M, as shown in fig. 5, are in front or behind tubes, C, D, according to requirement.



Figs. 4 and 5. Show the third form of apparatus used. The reason for having twin tubes is to provide for change in temperature of both large and small masses. The window is not shown in fig. 5.

One peculiarity of this form of suspension is that it never of itself comes to rest. For when the beam touches one tube at the end of a swing, it receives, by the tremors in the apparatus, enough energy to send it to the other end of its swing. This perpetual motion was counteracted by an arrestment (shown in the left side tube) worked by a magnet outside the vacuum. By this device the system was brought under control.

This form of apparatus was abandoned on account of an unexpected form of attraction which caused the masses, m, m, to rush to the walls of the vacuum vessel and cling there indefinitely. These forces are very strong and existed despite the fact that there was a complete " earthed " system of aluminium tubing lining the vacuum vessel and that the suspension was " earthed." After separate investigation this effect was attributed to radiometric-pressure, which cannot be avoided in this form of vacuum vessel.

In the final form of apparatus, to be next described, there are two distinct sets: (*a*) where the attracting masses are cylindrical; (*b*) where these are spherical. But as the latter type is more important, the following description applies to it throughout.

VI. Final Experiments.

1. *General Description.*—In this form one may be said to have at last attained some mastery over the investigation, so that details will be given. A glass tube, AB, (figs. 6 and 7) is 1200 mm. long, 50 mm. bore. It is supported near the top by two strong glass tubes, C, D, issuing from opposite sides of the main tube (see fig. 6). The top and bottom of the main tube are closed and there is a window, W, in front. Tube C, finishes with a platinum wire sealed in for the purpose of earthing the inside of AB; while tube D is the connection to the pumping system (see fig. 6).

2. *The Support for the Vacuum Tube.*—The glass tubes, C, D, rest on gimbals, CD, forming one axle, while a forked frame-work, V, of brass (fig. 8) carries the perpendicular axle, and itself is supported by being screwed to a stout beam. This beam, loaded by about 40 kilos. of lead weights, is carried by steel springs hung from the main scaffolding, and there are castor oil dash-pots to damp any chance vibrations which may be received from the ground.

The lower end of tube AB, socketted into a copper sleeve, *Cu* (fig. 8) is controlled by four setting screws mounted on a horizontal ring, *ab*. By this means AB can be set and held accurately vertical.

3. *The Torsion-head System.*—A brass frame-work (fig. 6) fits firmly by three pairs of brass springs into the upper part of tube, AB. These six spring points are tipped with solder to avoid the well-known danger of hard metal scratching the inner surface of the glass tube. There are two magnets in the frame-work; the lower one, m_1, carries the suspension by pin, p, which turns freely, but without shake, in the two thoroughfare bearings shown. The upper magnet, m_2, is mounted on a screw so that

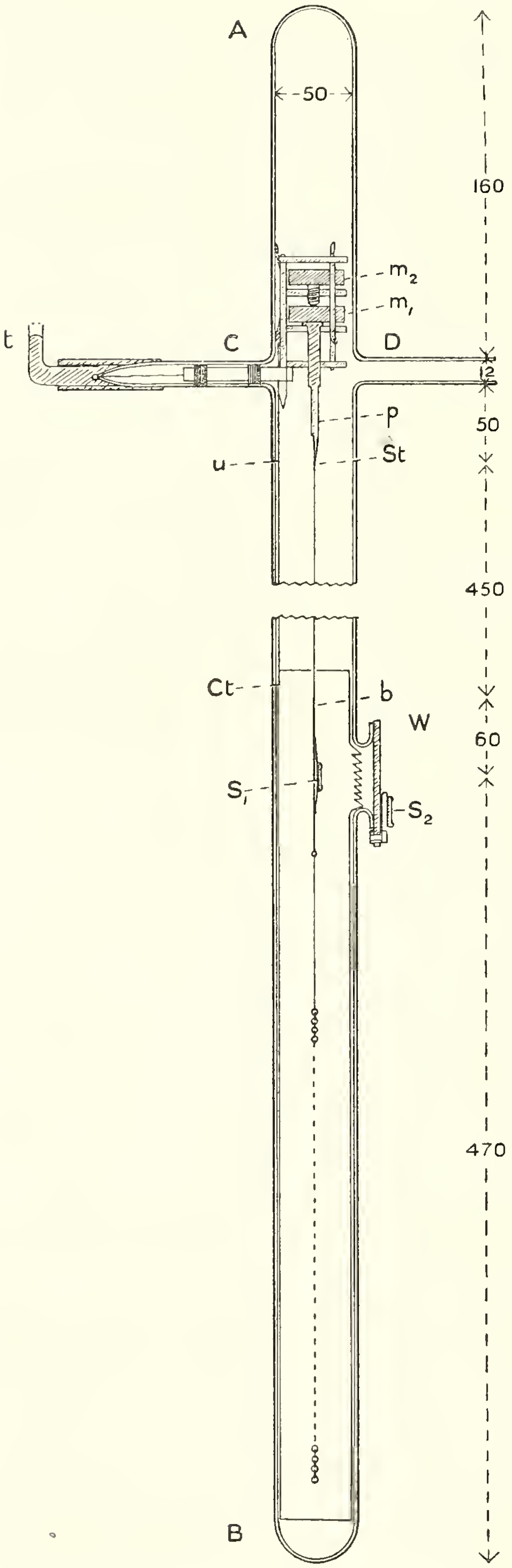


Fig. 6. Shows *m*, *m* in the form of chains.

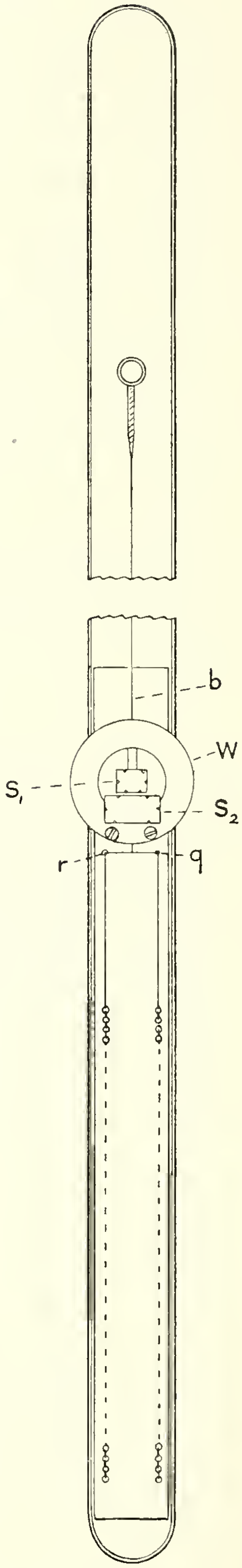


Fig. 7.

on turning one way on a vertical axis, it rises ; on turning the other way, it falls, and in so doing clamps m_1 by pressing hard on it. The horse-shoe electro-magnet, E (figs. 9 and 10), can be raised or lowered to operate m_1 or m_2. By this torsion-head arrangement the suspension can be set and clamped, wherever desired, *in vacuo.*

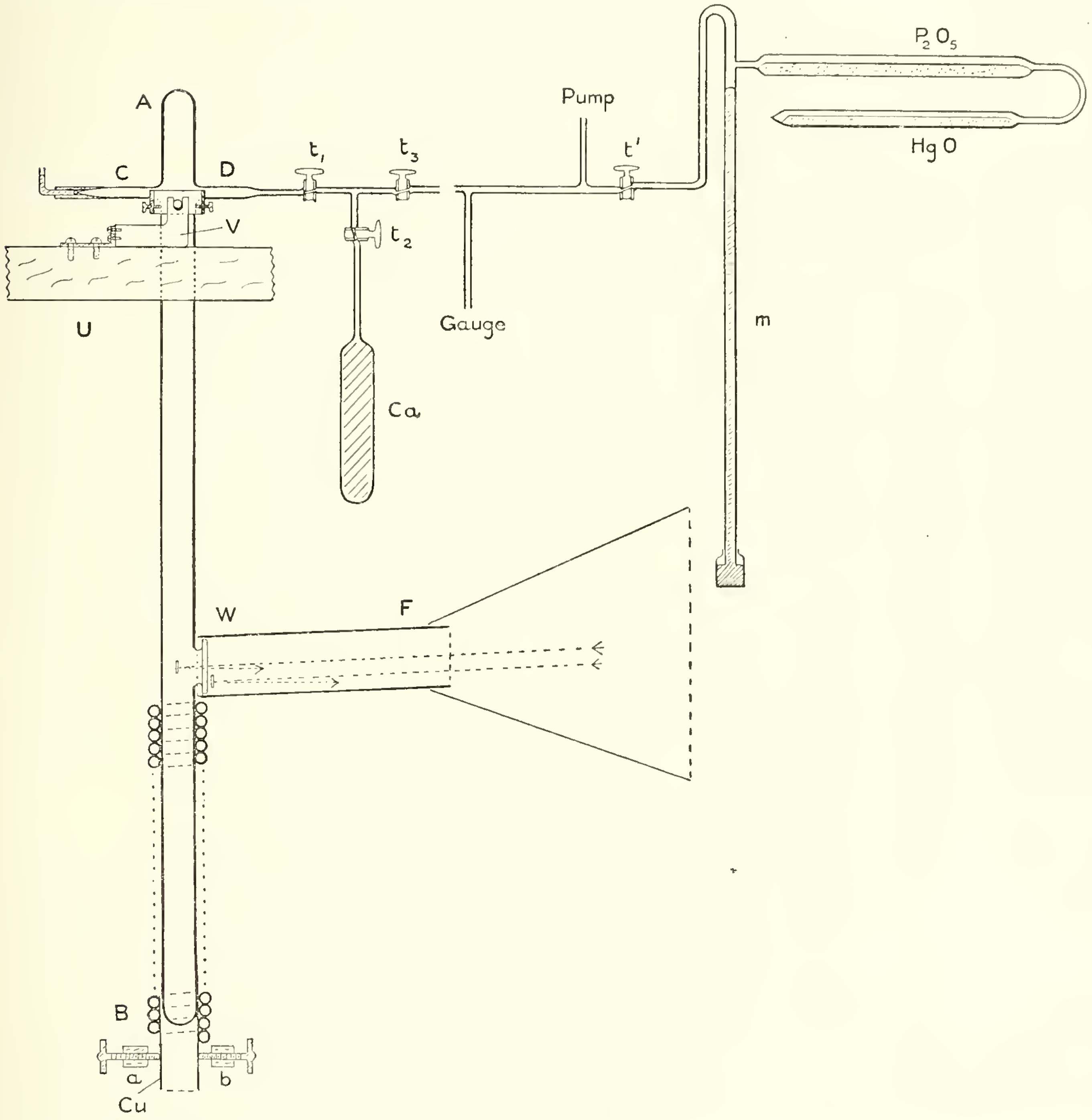


Fig. 8. Shows the tubing for evacuating and washing out with oxygen ; also the tube and funnel mounted on the window. The weight of this tube and funnel is carried by a wire attached to the main scaffolding. Part of the water-jacket, but no lagging, is shown at the lower end of tube AB.

4. *The Small Mass* (m, m) *System.*—The suspension is seen in the core of tube, AB (figs. 6, 7, 9, 10). The beam and the vertical wire, b, attached to its centre are of thin wire. The mirror, S_1, is enclosed in a case of thin foil and is so attached to the vertical wire that a fine inclination up and down can be made at will. The long copper or

silver tube, C*t*, inside AB, has a rosette hole (see fig. 6) cut in it at the window, W. By opening the rosette carefully it is possible to see mirror, S_1, whilst exposing little of the inside of the tube. Thus mirror, S_1 should be as far as possible screened from any radiometric action and from electrostatic charges on window, W. The actual small masses, *m*, *m*, are (in the form shown in the figure) made of chain, 30 cm. long, and are hung from the beam ends by very fine wire.

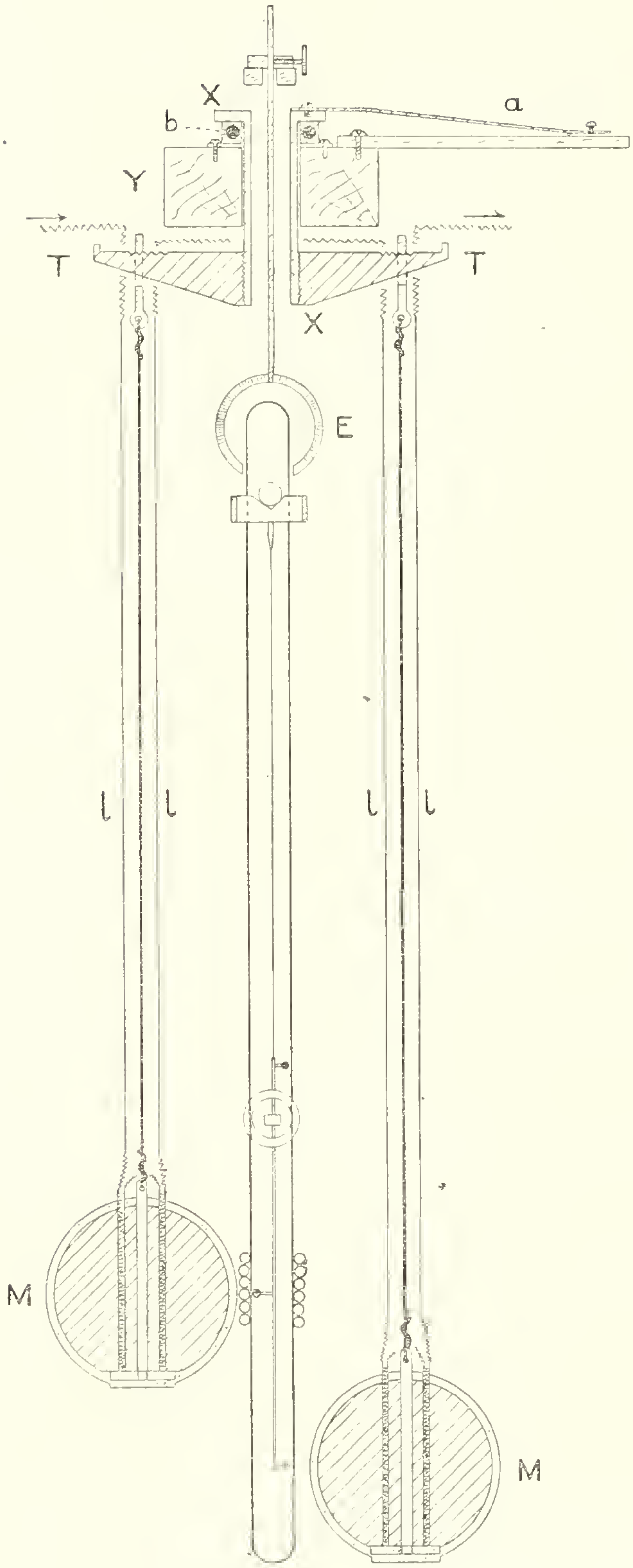


Fig. 9. Shows the final form as used with rigid suspension. (No wrappings shown.) ($\frac{1}{10}$ full size.)

The materials used throughout the system are wholly copper or wholly silver (both having very low permeability). The metal in each case was supplied by Messrs. Johnson, Matthey, in the form of wires and foils. They stated that the copper was electrically refined, prepared from precipitate. If any traces of foreign matter exist it would be minute particles of gold and silver. The silver should be absolutely "chemically pure." The torsion fibre (usually quartz, sometimes phosphor-bronze) is 480 mm. long, soldered to the beam system below and to the torsion-head above by Margot's solder.*

5. *The Optical Arrangement.*—The window glass, W, which is of selected plate glass, is sealed to the window flange by white wax. The window glass has two holes drilled in it by means of which a mirror, S_2, can be firmly fixed. This mirror which is adjustable in elevation shows the azimuth of the whole vacuum tube, and therefore that of the torsion-head, whereas mirror, S_1, shows the azimuth of the torsion beam. Thus the difference between the two telescope readings given by these two mirrors shows at any time the exact amount of torsion on the fibre with elimination of any error due to movement of tube or telescope.

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* See "Sealing Metals," by P. E. SHAW, 'Proc. Phys. Soc.,' Feb., 1912.

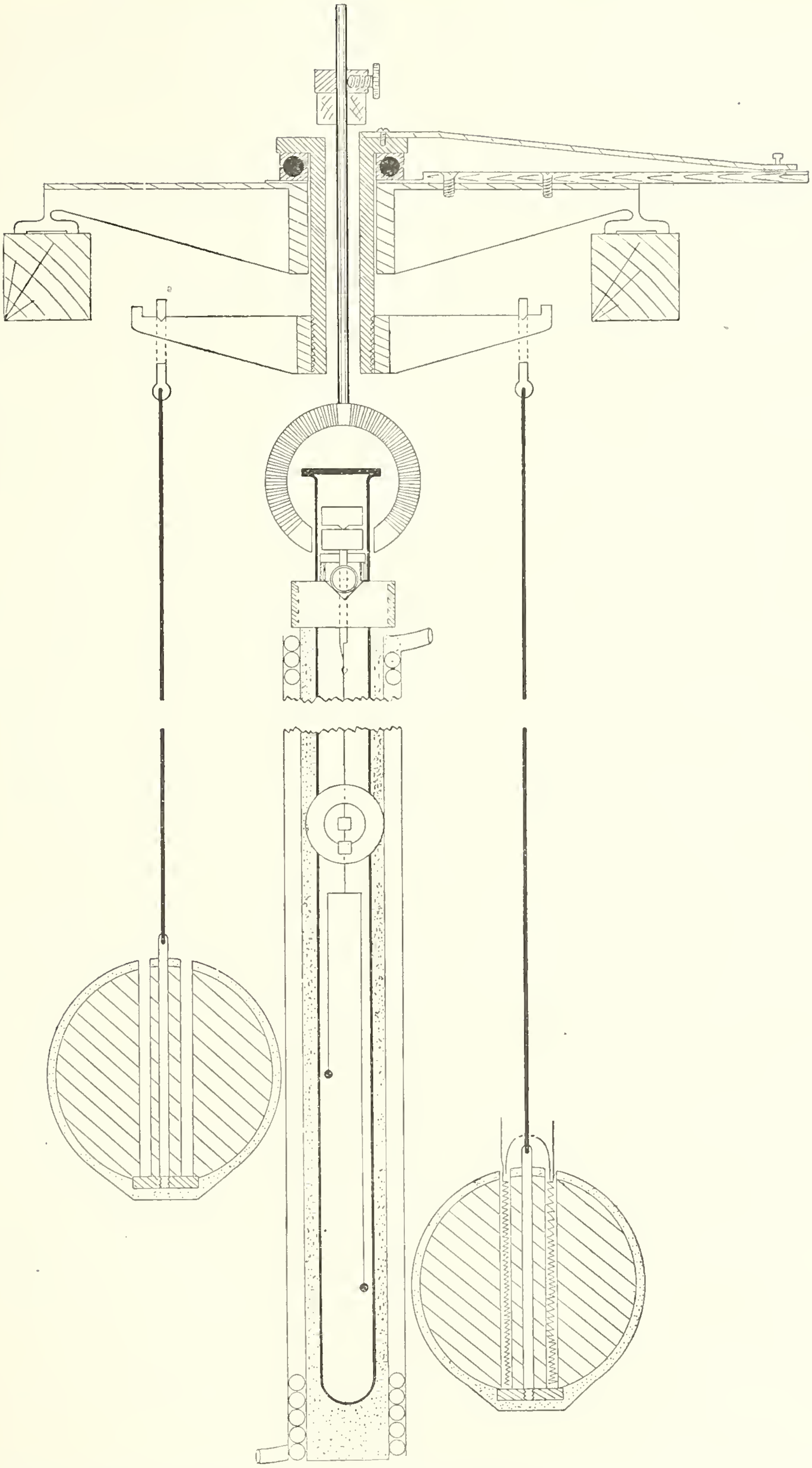

Fig. 10. Shows the final apparatus ($\frac{1}{6}$ full size) with limp suspension. This is the best arrangement. For clearness no lagging outside the water jacket is shown. The large amount cut out half way up the diagram will be appreciated by comparison with fig. 9, which has identical essential parts.

Facing the window, at $4\frac{1}{2}$ m., is an astronomical telescope of 7·5 cm. objective. Over the telescope and perpendicular to it are two scales, each illuminated by a glow lamp which is adjustable by pulleys and strings to any place on the scales, whilst the scales themselves can be moved vertically up and down and clamped anywhere.

Fig. 8 shows the connections for evacuating. A Gaede rotary pump and McLeod gauge are used. For washing out the vacuum, oxygen is obtained by heating mercuric oxide. *Ca* is the carbon tube and the three taps, t_1, t_2, t_3, well-made and properly treated with rubber, grease and wax, as explained elsewhere, are reliable for any length of time.

6. *The Large Mass* (M, M) *System.*—The two large spheres are of lead, 20 cm. diam., and weigh each about 47 kilos. I am much indebted to my colleague, Prof. C. H. BULLEID, for the great care and personal skill he put into the construction of these large masses. The special desiderata for them are : Freedom from air bubbles, freedom from iron, and accurate alignment in each, of three parallel brass tubes. A wooden pattern having been placed half-way in a moulding box, the latter was filled in with plaster of Paris. This made half the mould. The other half was made similarly with another box. The three brass tubes, full of plaster, were placed in position. The moulds were then roasted to dryness for several days before use. Commercial sheet lead only was used for the melting pot. As the molten lead was run into the mould great care was taken that cooling should proceed from below upwards. Hot cokes were laid on top of the mould, while the lead solidified at the bottom. The lead was puddled by a hot copper rod to dislodge all air bubbles. This process continued as solidification proceeded until finally the runner solidified. The spheres were of the same weight to 15 gr., so there was small likelihood of enclosed air. The tubes having been cleared of plaster and the spheres washed and swabbed with nitric acid to remove iron dirt, a stout carrier consisting of a copper rod, 1 cm. diam., screwing into a thick copper disc, was fitted into the central hole (figs. 9 and 10). The spheres are hung from the turn-table by copper wires. The two other holes in each sphere are fitted with tubes of asbestos and mica sheet rolled together ; into each is then placed a heating coil of nichrome (16 ohms resistance). The leads, *l*, *l* (fig. 9) for the heating coils are carried up to the turn-table. By this disposition these leading wires exert no influence on the hang of the spheres. The lead spheres are covered with two layers of cotton-wool, laid on in gores, for lagging. Over the cotton-wool is a layer of tin foil. In the experiments the whole heavy system can be rotated on a vertical axis with ease and smoothness on the ball-bearings shown in the figures.

7. *The Form of the Beam System.*—In fig. 12 are shown six forms of suspension, all of which have been exploited for these experiments. In each case the torsion fibre is attached to the top, and the mirror is shown as a small square. Any one of these forms would act well, if no tremors reached the suspended system from outside, but as vibrations do arrive from outside, some of them are unworkable in a vacuum vessel where there is no gas-damping.

It is a novelty to have a suspended system of limiting sensitiveness used in a high vacuum, so that the technical difficulties are new. To explain the action, consider form 3 (fig. 12). When a horizontal vibration reaches the torsion head of the suspending fibre, it passes down the fibre and reaches the top of the beam system, which at first experiences a simple horizontal vibration. Next, the vibration is carried down to the wires, *m*, *m*, each of which is set vibrating on a horizontal axis about its mass-centre. Soon we have a certain amount of pendular motion of two unequal periods. When at last the high frequency tremors of the fine wires and fibre have died out, there remain, very persistent in a high vacuum, the low frequency movements of *m*, *m*.

All the unsymmetrical systems, 3, 4, 5, and 6, are troublesome for these reasons, whereas forms 1 and 2, give relatively little trouble. But the unsymmetrical form is, for a short beam, as shown by C. V. Boys, indispensable for sensitiveness. Working in the heart of a large city, I failed with Nos. 3, 4, 5, and 6 after long trial, and only succeeded with No. 7 (see fig. 10) by allowing in the vacuum chamber a small amount of air for damping purposes.

It might be thought that some form of damping would be possible so as to render any beam system workable. Of the known damping methods (1) gas-friction and (2) liquid-friction are inadmissible in a high vacuum, but (3) electro-magnetic damping which I tried in several ways, failed always. It is impossible to have any magnetic material on the beam, and it is risky to have, say, a closed copper wire circuit carried on the beam. But there is one other damping method possible, viz., (4) rolling friction. I have used chains extensively as in No. 2 (fig. 12) and have found that the rolling of one link on the next brings in rolling friction to damp out tremors. Such a chain system acts very well in high vacuum, even in a very disturbed laboratory. (See results in Table I.)

8. *Sealing Materials Used.*—The use of waxes in vacuum vessels is now well understood. For joining the optical window and the top glass plate to the vacuum tube (see figs. 9 and 10) I use (*a*) Faraday cement, or, better (*b*) a white "vapour-free" wax (supplied by Lilliendahl, Neudietendorf); these both seem much tougher than sealing wax or shellac. Then there is (*c*) a soft red sealing wax sold commercially. I never trust any ground glass joint, or any mercury-trap joint, or any platinum seal, but in all cases melt some of this wax outside the junction, and also on the top and bottom of all ground glass taps to ensure against leakage. (*d*) Ramsay's tap grease is used to lubricate the taps. At moderate temperature, say 60° C., vapour comes off freely from (*a*) and (*b*), so such high temperatures have to be avoided for these seals. (*c*) and (*d*) are by no means vapour-free at ordinary temperatures, but the only way in which they come in contact with the vacuum is on the vacuum taps; and the small amount here used soon becomes vapour-free in the vacuum, without serious detriment to the latter.

There are many joints in a Gaede mercury pump which become leaky periodically. It is well to serve all of them with some melted wax (*c*).

9. *Preparation of the Apparatus for an Experiment.*—Suppose in this instance a copper internal system is to be used. The long glass tube (fig. 6) as received from

the glass blowers is open at top, A, and has the two side tubes welded on and the window flange prepared. First the inside is given a thick coat of silver up to about 20 cm. above the window flange. This coating reduces radiation during the experiment and enables one to thoroughly "earth" that part of the vacuum surrounding the suspended system. The central portion, DW, of the main tube is wrapped externally with asbestos paper, and over that eureka wire is wound to act as a heating coil. The brass tube already mentioned, with platinum wire at one end, is inserted in tube C, and the glass sealing on tubes C and D is completed. A mercury seal *t* outside the platinum seal is shown. The copper inner sheath is lowered into the main tube and the rosette at the window opened; the strap, U, which carries the sheath, is fitted to the brass tube in C to keep the sheath in position. The optically-true window is now sealed on to its flange.

The torsion system is next prepared. From a frame holding some hundred quartz fibres of 60 cm. length and suitable diam. (*i.e.*, from 21μ to 15μ diam.), four or five have been chosen several days before and all have been attached to a horizontal bar and loaded with a weight about 25 per cent. more than the actual load used in the experiment. It is impossible to predict to within 50 per cent. what a quartz fibre of known diameter will carry. A fibre may sustain a load for several hours or even a day and then break without external shock being applied. Hence every fibre is given a three or four days' test before use. The finest fibre which has stood the test is fixed by Margot's solder to the torsion head above and to the beam system below, which in the present case we will suppose has form 2, fig. 12. The whole suspended system, except the small mirror, is of the purest obtainable metal, say copper. After the beam system has been put together, but before the fibre is attached, the whole of it, except the mirror, is immersed in nitric acid, and then thoroughly washed, to remove any trace of iron which may have become attached by tools or by the hands during construction.

It is important to see at this stage that the mirror is properly inclined to the vertical as no adjustment of it can be performed later in the vacuum.

Next the torsion system, *i.e.*, torsion head, fibre and beam system, are lowered with the utmost care to prevent breakage of the fibre, into the vacuum tube till the torsion head rests socketted in a hole prepared in the brass tube, C (fig. 6). Several asbestos paper discs are placed on the top of the torsion head frame to keep the latter cool in the next stage. The top of the main glass tube is next sealed. This sealing of a 5 cm. tube requires two operators, one on each side with a blowpipe. Care is taken to keep heat from the torsion head just below. In later experiments a glass plate was waxed on the top (see figs. 9 and 10). The vacuum tube and contents is now cautiously removed and set on its gimbals in the supporting frame. The adjusting screws below are so set that the suspended system swings free of the tube walls so as to be ready for the experiment. The vacuum side tube, D, is sealed to the carbon tube, C*a*, and this to the pump (fig. 8).

Preparation of the Vacuum.—A heating coil of eureka wire is pushed up over the lower section, WB (fig. 6), and another put on the upper section, AC, of the main tube. The middle section, as stated, is already wired. Also the whole of the glass tubing connecting to the pump and McLeod gauge, and the oxygen plant are similarly wired. The large carbon tube has a special heating coil of several layers designed to attain a high temperature. The whole system of heating coils is put in series with a lighting circuit and a current of 3·5 amperes is developed. The injector pump and Gaede pumps are started. The temperature attained by various parts is arranged according to requirement. The lower part of the vacuum tube, WB, attains a temperature of 130° C. The upper tube containing the soldered joints is not raised much above 100° C, while the sealed-on plates are kept as a rule below 60° C. Any small condensation of vapour on the cool window can be carefully removed by placing a carbon glow-lamp in front of it for a short time. The carbon tube is raised to 340° C., as shown by a platinum thermometer placed between it and the heating coil. The double process of heating and exhausting proceeds for five days (say 50 working hours), during which time the McLeod gauge should show steadily improving vacuum. At night, when the evacuation is stopped, the taps have to be shut in such order that the rapidly cooling main tube shall not receive vapour from the hot carbon. On the last day of exhaustion the vacuum would be, say, 10μ, when the temperature is full everywhere. Then the vacuum is washed out, once or twice, with oxygen to remove traces of the less absorbable gases, nitrogen, helium, argon. Finally on cutting off the heat the pressure will drop to the smallest readable by the McLeod gauge, say, $0{\cdot}05\mu$. The carbon will then be about 200° C. The taps are closed till, when temperature everywhere is normal, the taps t_1 and t_2 are opened, and all three taps have warm siegelwachs run over them. The glass between tap t_3 and the pump is sealed off.

Evacuation being finished, the apparatus has to be prepared for the experiment.

Adjustments.—First, the torsion head is turned so that the beam mirror, S_1 (figs. 6 and 7), exactly faces the window; the electro-magnet, E, is lowered until its poles are level with the torsion head magnet, and by rotation of E the torsion head is brought to the correct azimuth. By raising E to the level of the clamping magnet and again suitably rotating the former, the inside magnet is brought down to bear hard on the torsion head and thus fix it. Under this condition the mirror, S_2, fixed to the window will exactly stand for the position of the top of the fibre. Rotation of one always accompanies that of the other, both being rigidly attached to the main tube.

Next, the loose heating coils are stripped off and the whole vacuum system, including the connecting tubes wrapped in several layers of cotton wool. Before, however, the cotton wool is put on two platinum thermometer wires are wrapped on the glass of the vacuum tube, one above, and one below the window, and compensating copper wires are arranged.

In providing a water-jacket to screen the vacuum tube from the hot masses, M, M, it must be borne in mind that temperature should be uniform radially rather than longitudinally in the long tube; for radiometric pressure, not convection, is likely to be the main gas trouble. The plan adopted is to have water tubes wound over the whole vacuum tube up to the level of the top of the torsion fibre. Similar metal water tubes are wound over the tube covering the window. In fig. 8, the covering tube, but not the water tubes, are shown. There is a space of about 6 cm. near the window on the long tube which cannot be wrapped with metal tube, so rubber tube is used, with a specially large amount of closely-packed cotton-wool, in this region. Thus we have several layers of cotton wool both within and outside the water helix; while the hot spheres, M, M, are themselves covered doubly in cotton-wool and then in tin-foil.

Water from the tap passes to the window region and branches into four parts, viz.: (*a*) the upper tube; (*b*) the lower tube; (*c*) the window cover; and (*d*) the window region. Each section thus receives water at one and the same temperature.

After leaving the water-jacket, the water passes into vessels where its temperature can be watched. A Page thermostat was attached, but proved unnecessary.

Next, the whole system of M, M, with the turn-table above (see figs. 9 and 10) is set co-axial with the torsion fibre, *i.e.*, until masses, M, M, clear the wrapped tubes equally all round; M, M being so far apart as to just clear the water-jacket everywhere. The heating coils of nichrome inserted in insulating tubes in M, M (see fig. 9) are connected in series with a 200-volt circuit, the leads being taken right up the copper suspending wires to the turn-table to avoid any hampering of the free motion of the heavy mass system.

The last adjustment is to bring the beam to rest. The period of the beam may be anything from 2 mins. to 10 mins. The angle of rotation after the above violent adjustments is sure to be considerable and in high vacuum the swings are practically undamped.

There are three ways of reducing the swing:—

(1) By moving the vacuum tube to one side and so bringing it against the beam system. Sometimes this succeeds, but great judgment and timing are required or the amplitude will be increased instead of decreased by the contact.

(2) Unclamp the torsion head and rotate the magnet, E, and so time the movement of the head that the torsion of the fibre is always acting against the motion of the beam. The head must be left clamped finally.

(3) Gravitational damping by moving large masses, M, M, to always oppose the motion of the beam system. This method is too weak to be effective, except as a finishing touch to reduce the swing when it is already small, say, 5 degrees of arc.

The process of damping the swing may take many hours, but it must be done so that finally the mirror when at rest would face the centre of the scale (of 500 mm.) which is placed about 5 m. away and immediately over the large reading telescope.

The apparatus is now ready, but it is found that no accurate work can be performed for several days after the rough handling incidental to the adjustments. Since the fibre has a factor of safety of only 50 per cent. or so, great care is taken to avoid any jolts to the apparatus; the movements given to the beam are due not to jolts, but to the occasional contact of the torsion system with the vacuum tube.

A drift of zero is found to occur, perhaps due to small elastic after-effect following the recent heating. I have found that in some unsymmetrical systems *in vacuo*, the zero never comes to rest, since the violent tremors set up by recurrent outside vibrations cause either constant strains in the fibre, or constant unbalanced pendular oscillations. However, under favourable conditions, readings can commence in three days.

The next step is to ascertain the best angle at which the turn-table must be set for maximum deflection of the beam in the A and B positions (see fig. 11). For spherical masses the formula given by C. V. BOYS[*] is very useful, viz. :—

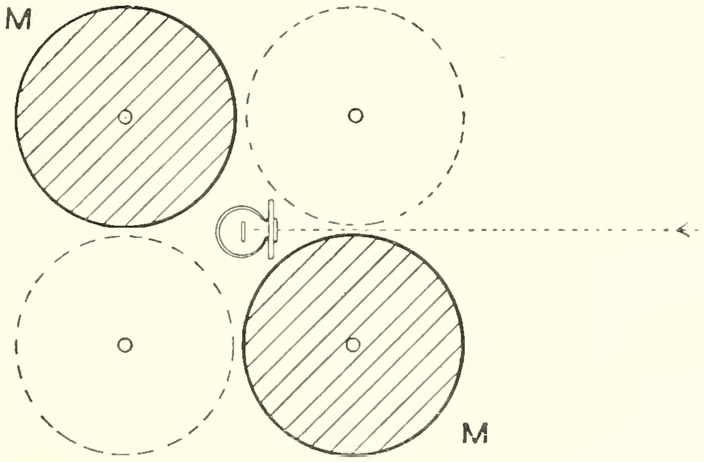

Fig. 11. This plan section shows the disposition of the large masses in the A and B positions.

$$\cos^2\theta + \frac{a^2+c^2}{ac}\cos\theta - 3 = 0,$$

where θ is the angle for maximum attraction,

c is distance between centre of beam and that of large mass ;
a is half the length of the beam.

Determine θ in terms of a and c. But as it is most important both for sensitiveness and accuracy to have the exact positions of maximum attraction, the matter is settled by trial, and when the best positions on the dial of the swing table are found stops are placed so that in the coming experiment the same angle is used in every case.

Before commencing actual readings, it must be decided whether or not the carbon tube is to be used cooled by liquid air. In the earlier experiments, liquid air, boiled under reduced pressure to give a temperature of −200° C., was used. Later this was given up, as the very exhausted carbon at ordinary temperature acted well enough.

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[*] 'Proc. Roy. Soc.,' 46, 1889.

Supposing the carbon is not to be cooled, it is given layer after layer of cotton wool and is otherwise screened from heat rising from below.

10. *Description of Experiments.*—At the commencement of readings, set the masses M, M, at position A (shaded in fig. 11). Watch the beam mirror with the telescope and set down the extreme readings as the beam swings. When three such readings have been taken, rotate M, M to position B, and proceed as before. For every position, A or B, the tube mirror reading (S_2, fig. 6) is taken by the telescope.

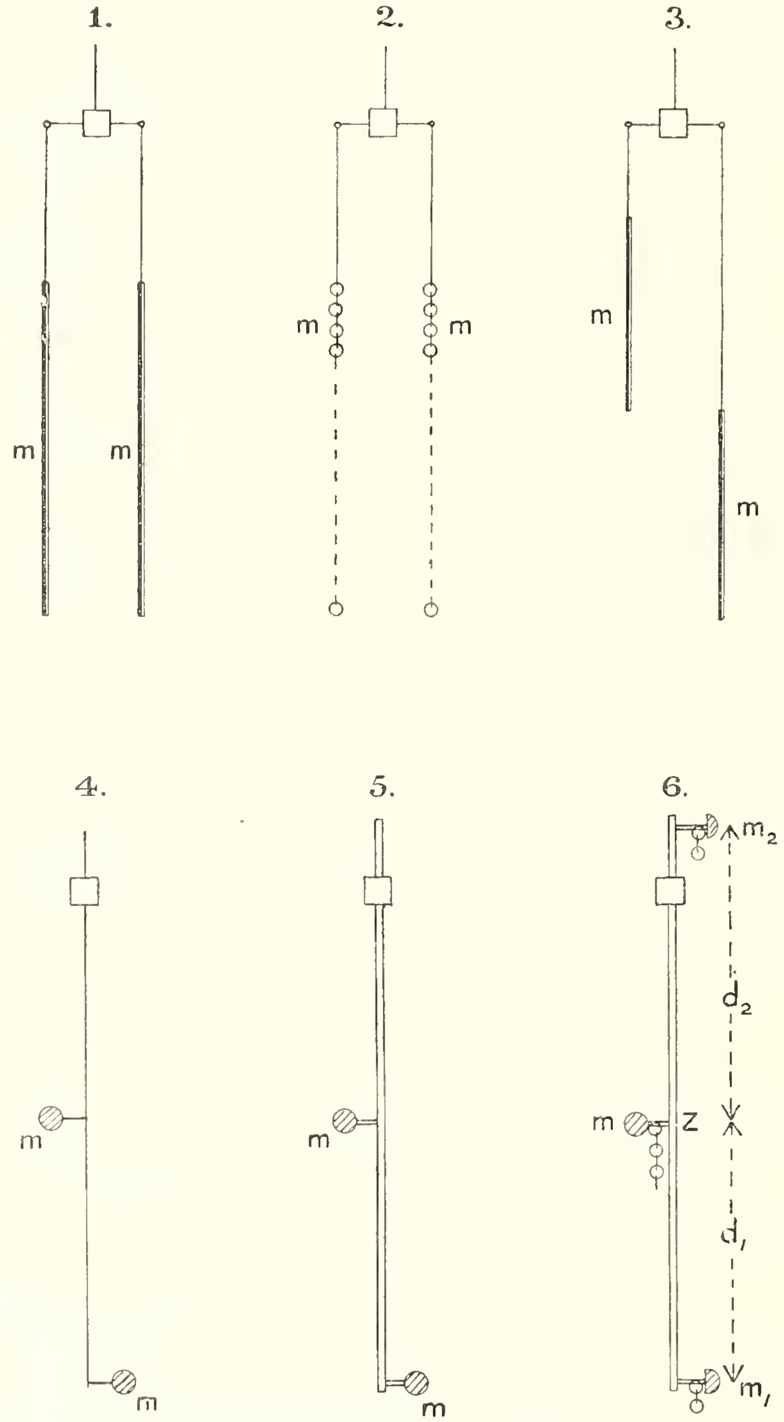

Fig. 12. Various forms of suspension used.

In Table I. are shown the results of an experiment with cylindrical masses.

Table I.—June 23, 1914. Silver Chains (m, m.). Lead Cylinders (M, M). Vacuum Pressure, 1·0μ. Oscillation Period, 252 minutes.

Position.	θ_L.	θ_T.	L.	R.	Mean.	T.R.	Corrected mean.	Range.	Mean range.
					I. Steady Cold.				
	° C.	° C.							
A	17	17·0	191·8 192·1	263·8	227·8 227·9	94·5	227·85		
								57·48	
B			132·7	208·1 207·8	170·4 170·25	94·45	170·37		
								57·63	
A			193·8 194·0	262·0	227·9 228·0	94·45	228·0		
								57·68	57·57
B			133·7	207·0 206·7	170·35 170·20	94·45	170·32		
								57·48	
A			187·8 188·0	267·7	227·7 227·8	94·45	227·8		
								57·58	
B			136·8	203·7 203·4	170·25 170·10	94·45	170·22		
					II. Steady Hot (after heating for five hours).				
B	210	18·5	133·4	213·5 213·3	173·45 173·35	94·7	173·20		
								57·70	
A			194·9 195·3	267·2	231·05 231·25	94·95	230·90		
								57·65	
B	212		139·0	208·6 208·4	173·80 173·70	95·2	173·25		
								57·87	
A		18·5	193·3 193·6	269·4	231·35 231·50	95·0	231·12		
								57·65	57·67
B			137·6	210·1 209·8	173·85 173·70	95·0	173·47		
								57·60	
A			196·9 197·0	265·8	231·35 231·40	95·0	231·07		
								57·72	
B			139·0	209·0 208·8	174·0 173·9	95·3	173·35		
								57·52	
A	212	18·5	193·6 193·9	269·2	231·4 231·55	95·3	230·87		

In and after column 4, all readings are expressed in millimetres.

TABLE I. (continued).

Position.	θ_L.	θ_T.	L.	R.	Mean.	T.R.	Corrected mean.	Range.	Mean range.
III. Falling Temperature.									
	° C.	° C.							
B	177	18·5	137·3	210·2 209·8	173·75 173·55	95·70	172·65	57·85	57·65
A			194·0 194·0	269·3	231·65 231·65	95·75	230·50	57·50	
B	160		138·7	209·6 209·4	174·15 174·05	95·80	173·0	57·65	
A	152		198·0 198·2	265·3	231·65 231·75	95·80	230·65		

In and after column 4, all readings are expressed in millimetres.

Column 1 shows the position of masses, M, M. The next two columns have the temperatures of the masses, M, M, and of the vacuum tube, respectively. Columns 4 and 5 give the extreme left and right scale readings, as the beam swings. Column 6 shows the arithmetic mean of the two preceding column readings, while column 8 shows this value corrected for change, if any, in the tube reading (column 7). The rest is obvious, heat being applied as already explained. There are three sections in the experiment, I., steady cold; II., steady hot; and III., falling hot. By combining I. and II. we obtain as temperature effect

$$\alpha = +0{\cdot}8 \times 10^{-5} \text{ per } 1^\circ \text{ C.}$$

By combining I. and III., we find a like result.

It will be observed that the vacuum is high; the pressure $1{\cdot}0\ \mu$ is calculated from the damping of the oscillations.

Only this one example for cylinders will be quoted in full, for, though the readings are steady, the subsequent work with spheres is more sensitive and more reliable in general.

In Table II. are entered the results of an experiment with spheres. Here we have seven sections, the last half, hot and cold, being taken ten days after the first. It will be seen that the interval of rest makes no appreciable difference in the result. Column 2 shows the time, column 3 the reading of the tube (reference) mirror. The fourth column has the extreme scale readings right and left as they occur, and the

Table II.—July 27, 1915. Silver Balls (m, m). Lead Spheres (M, M).
Vacuum Pressure, 14 mm. Oscillation Period, 280 minutes.

Position.	T.	T.R.	R.	Amplitude.	Z.	Range.	Mean range.	θ_L.	θ_{LT}.
A	4.11	345·0	37·5 267·8 112·5 216·8	230·3 155·3 104·3	175·0 174·9 (174·95)			° C. 17	° C. 13·0
						200·75			
B		345·35	493·0 297·5 428·9 340·5	195·5 131·4 88·4	376·1 376·0 (375·7)				
						200·85	200·85		
A		345·1	53·3 257·3 119·5 212·2	204·0 137·8 92·7	175·0 174·9 (174·85)				
						200·95			
B		345·4	425·9 342·9 398·8 361·0	83·0 55·9 37·8	376·3 376·2 (375·8)			17	
Heat at 8.2. Stop Heat at 10.2.									
B	10.23	345·45	241·8 466·8 315·2 417·3	225·0 151·6 102·1	376·2 376·2 (375·75)			206	12·3
						201·05			
A		345·0	19·4 279·2 104·4 222·0	259·8 174·8 117·6	174·7 174·7 (174·7)			198	
						201·25			
B		345·35	476·9 308·6 421·8 345·7	168·3 113·2 76·1	376·3 376·3 (375·95)			191	
						201·25			
A	10.55	345·0	52·7 256·7 119·6 211·8	204·0 137·1 92·2	174·7 174·7 (174·7)			183	
						201·3	201·25		

Readings in columns 3, 4, 5, 6, 7, 8 are in millimetres.

TABLE II (continued).

Position.	T.	T.R.	R.	Amplitude.	Z.	Range.	Mean range.	θ_L.	θ_{LT}.
Heat at 8.2. Stop Heat at 10.2 (continued).									
								° C.	° C.
B	11.6	345·3	482·1 305·1 424·1 344·1	177·0 119·0 80·0	376·3 376·3 (376·0)			174	
						201·35			
A	11.22	345·0	40·4 264·7 114·0 215·6	224·3 150·7 101·6	174·6 174·7 (174·65)			163	
						201·25			
B		345·3	492·9 297·9 428·8 340·8	195·0 130·9 88·0	376·2 376·2 (375·9)				
						201·15			
A	11.50	344·95	50·3 258·4 118·3 212·7	208·1 140·1 94·4	174·7 174·7 (174·75)			148	12·4
Pause.									
B	3.21	345·2	483·9 303·5 425·0 343·3	180·4 121·5 81·7	376·1 376·1 (375·9)				
						200·8			
A		344·85	45·7 262·1 116·4 214·1	216·4 145·7 97·7	175·0 174·9 (175·1)			71	
						200·8	200·85		
B		345·15	464·8 316·5 416·0 349·2	198·3 99·5 66·8	376·1 376·0 (375·9)				
						201·0			
A	3.54	344·8	52·0 257·5 118·9 212·3	205·2 138·6 93·4	174·7 174·7 (174·9)			66	

Readings in columns 3, 4, 5, 6, 7, 8 are in millimetres.

TABLE II. (continued).

Position.	T.	T.R.	R.	Amplitude.	Z.	Range.	Mean range.	θ_{L}.	θ_{LT}.
				Pause.					
B	7.2	345·0	467·2 314·3 417·4 348·0	152·9 103·1 69·4	375·9 375·9 (375·9)			°C. 43	°C.
						201·1			
A		344·7	53·0 256·3 119·5 211·6	203·3 136·8 92·1	174·5 174·5 (174·8)				
						200·85			
B	7.24	344·95	477·0 307·6 421·6 344·9	169·4 114·0 76·7	375·7 375·7 (375·75)		200·95	41	
						200·9			
A		344·7	269·0 110·8 217·5 145·7 193·9	158·2 106·7 71·8 48·2	174·5 174·6 174·5 (174·85)				
						201·0			
B	7.52	344·95	461·2 318·5 414·3	142·7 95·8	375·8 (375·85)			40	
				Pause for 9 days. August 4, 1915.					
A	9.50	342·7	61·5 246·4 122·2 205·7	184·9 124·2 83·5	172·1 172·1 (172·1)			17	
						200·85			
B		343·0	473·0 306·2 418·3 342·8	166·8 112·1 75·5	373·3 373·2 (372·95)				
						200·7			
A	10.19	342·7	47·9 256·0 115·9 210·0	208·1 140·1 94·1	172·3 172.2 (172·25)		200·80		
						200·7			
B		343·0	469·6 308·3 417·0 343·9	161·3 108·7 73·1	373·2 373·3 (372·95)				
						200·8			
A	10.45	342·75	35·0 264·6 110·1 214·0	229·6 154·5 103·9	172·2 172·2 (172·15)			17	13·5

Readings in columns 3, 4, 5, 6, 7, 8 are in millimetres.

TABLE II (continued).

Position.	T.	T.R.	R.	Amplitude.	Z.	Range.	Mean range.	θ_L.	θ_{LT}.
Start Heat at 11.5. Stop Heat at 1.5.									
								° C.	° C.
A	2.5	343·0	46·8					180	13·1
			257·0	210·2					
			115·2	141·8	172·3				
			210·7	95·5	172·3				
					(172·0)				
						201·2			
B		343·2	480·8					173	
			302·0	178·8					
			422·0	120·0	373·8				
			341·0	81·0	373·6		201·2		
					(373·2)				
						201·2			
A	2·27	342·95	51·2					166	
			253·7	202·5					
			117·5	136·2	172·3				
			209·0	91·5	172·2				
					(172·0)				

Readings in columns 3, 4, 5, 6, 7, 8 are in millimetres.

fifth column shows the amplitude of swing. The next column has the rest position (Z) calculated from the formulæ

$$Z = c - \frac{(c-b)^2}{(a-b)+(c-b)} = b + \frac{(c-b)^2}{(c-b)+(c-d)}$$

where a, b, c, d, are the readings in order in column 4. These formulæ are based on the supposition that damping is so small that the successive amplitudes may be considered to be in geometric progression. The numbers in brackets in column 6 denote the mean value of Z corrected for the change, if any, in the reading of the reference mirror. The seventh column shows the range, *i.e.*, the corrected scale reading when passing from A to B position or *vice versa*. The eighth column has the temperature of the lead spheres as given by mercury thermometers. The last column shows the temperature of the outside of the vacuum tube below the window, as given by a platinum thermometer. The change in temperature varies up and down without much connection with the temperature of masses, M, M. Likewise the change of temperature in the water leaving the water-jacket amounts to 0·25° C., due mostly to change in temperature of the tap water. These small changes sometimes up, sometimes down, cannot influence the general result. As a rule the water temperature is very steady for long periods. After a set of readings at low temperature, the thermometers are removed from the lead spheres and the nichrome heating coils are substituted. When, after say two hours, the lead spheres are at a high temperature, the thermometers are again substituted for the coils, so that for the set of hot readings all the conditions are exactly the same as for the cold readings, except as regards the raised temperature in masses M, M. A graph is given for the result. The effect is

$$+1{\cdot}2/10^5 \text{ per } 1^\circ \text{ C.}$$

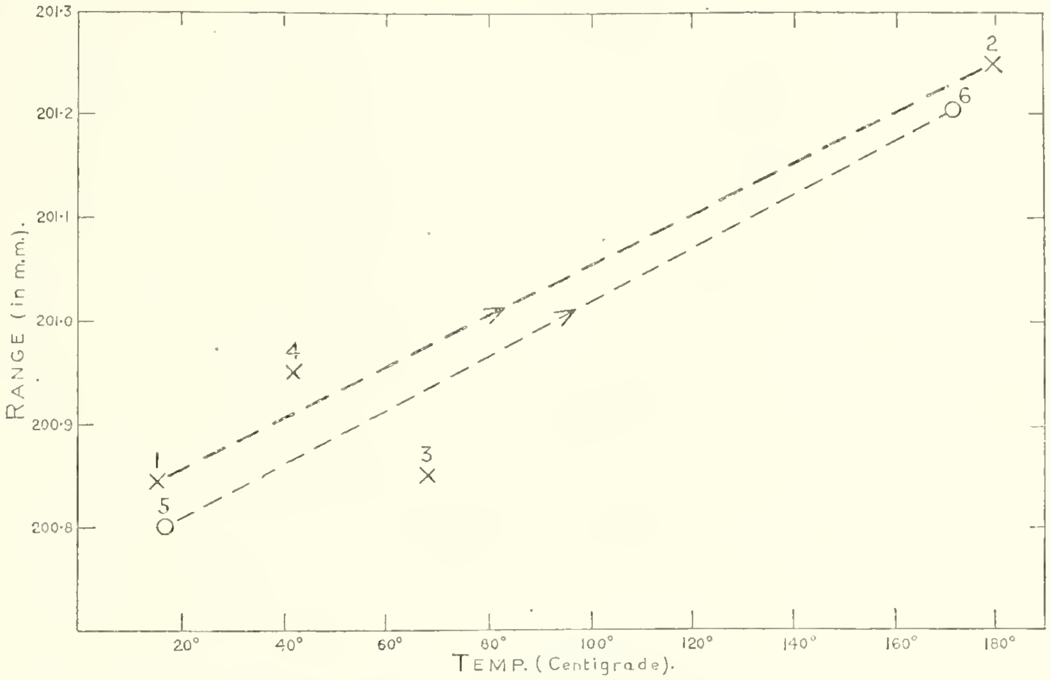

Fig. 13. Graph for Table II. The crosses show the first series of readings, the numbers being in order. The circles show the second series.

Table III. is another instance. It differs in some details from the preceding table. In particular, the fourth column consists of only two entries at each A, B position. These are two consecutive extreme scale readings. Call them a, b. Then if Z be the rest position, we have, supposing geometrical progression in the amplitudes,

$$Z = \frac{ad + b}{1 + d}$$

where d = decrement (*i.e.*, ratio of one swing to the preceding one).

The value of d is found independently before or after the experiment. The method used here has several advantages over the usual method of taking three or more extreme scale readings, viz. :—

(1) The experiment is shortened. It may be very tedious when, as here, each half-swing takes 160 secs., and the whole series lasts 6 to 8 hours.

(2) It is important when the large spheres are hot that they should remain as short a time as possible at any one part of the vacuum tube. We reduce the time of rest at any place by this process to about two-thirds of the least time possible by any other means.

TABLE III.—August 21, 1915. Silver Balls (mm.). Lead Spheres (M, M). Vacuum Pressure 14 mm. Oscillation Period 280 minutes.

Position.	T.	T.R.	R.	Z.	Range.	Mean range.	θ_{L}.	θ_{LT}.	θ_{HT}.
							° C.	° C.	° C.
B	11.55	*353·7*	402·7 313·9	349·6			18		
					175·45				
A		353·7	71·4 243·2	174·15					
					175·60				
B	12.7	353·7	464·0 273·0	349·75		175·50		13·5	13·5
					175·45				
A		353·7	85·6 233·9	174·3					
					175·45				
B	12.18	353·7	442·6 287·4	349·75			18		
Heat for 35 minutes.									
B	1.37	354·15	407·7 311·0	349·9 (349·45)			88	13·5	
					175·55				
A		354·15	75·4 240·8	174·35 (173·9)			86		
					175·75	175·65			
B	1.47	354·15	436·9 291·8	350·1 (349·65)			84		
					175·70				
A		354·2	80·9 237·15	174·35 (173·95)			83		13·5
Heat for 30 minutes.									
B	3.36	354·6	410·4 311·0	350·95 (350·05)			216		
					176·2				
A		354·6	77·3 240·5	174·85 (173·95)			210		13·6
					175·9	175·95			
B		354·5	443·0 288·6	350·65 (349·85)			206	13·5	
					175·75				
A	3.53	354·5	83·4 236·3	174·9 (174·1)			202		

Readings in columns 3, 4, 5, 6, 7 are in millimetres.

TABLE III. (continued).

Position.	T.	T.R.	R.	Z.	Range.	Mean range.	θ_{L}.	θ_{LT}.	θ_{HT}.
Heat for 90 minutes.									
							°C.	°C.	°C.
B	4.27	354·55	436·7 292·8	350·65 (349·8)			215		13·8
					176·0				
A		354·6	81·7 273·3	174·7 (173·8)			211	13·5	
					176·3	176·1			
B		354·55	440·1 291·0	350·95 (350·1)			206		
					176·05				
A		354·55	84·0 236·0	174·9 (174·05)					
Heat for 30 minutes.									
B	5.30	354·6	415·0 307·5	350·7 (349·8)			233		
					175·95				
A		354·6	76·9 240·5	174·75 (173·85)			227		
					175·95	175·9			
B		354·5	438·5 291·5	350·6 (349·8)			222		
					175·7				
A		354·5	81·8 237·4	174·9 (174·1)			216		
Heat for 40 minutes.									
A	6.48	354·1	75·9 240·9	174·6 (174·2)			246	13·6	
					175·8				
B		354·1	436·4 292·6	350·4 (350·0)			242		
					175·95				
A		354·05	72·6 242·8	174·4 (174·05)		175·95	237	13·6	
					175·95				
B		354·0	452·7 281·5	350·3 (350·0)			231		
					176·0				
A		354·0	88·0 232·3	174·3 (174·0)			224		

Readings in columns 3, 4, 5, 6, 7 are in millimetres.

TABLE III. (continued).

Position.	T.	T.R.	R.	Z.	Range.	Mean range.	θ_L.	θ_{LT}.	θ_{HT}.
Pause.									
B	8.55	353·25	442·2 287·1	349·45 (349·9)			°C. 143	°C. 13·7	
					175·5				
A		353·3	71·7 242·7	174·0 (174·4)			139		
					175·55				
B		353·3	444·1 286·0	349·55 (349·95)		175·65	136		
					175·7				
A		353·35	85·5 233·3	173·9 (174·25)					
					175·8				
B		353·35	445·6 285·3	349·7 (350·05)			130		
Pause.									
B	11.7	353·5	424·0 299·5	349·55) (349·75)			90		
					175·75				
A		353·5	79·7 237·1	173·8 (174·0)		175·75	88		
					175·75				
B		353·5	439·3 289·2	349·55 (349·75)					

Readings in columns 3, 4, 5, 6, 7 are in millimetres.

There are no temperatures for water shown in this table. Long experience shows that the temperature of the outflow remains sufficiently steady, and the scale readings settle down provided the water has been set running abundantly for an hour or two previously. The rate of flow of water remains constant, say 5 litres/minute, throughout the whole experiment. A graph is given of results in Table III. The temperature effect works out as

$$\alpha = +1{\cdot}3 \times 10^{-5} \text{ per } 1^\circ \text{ C.}$$

The above three examples given are among the most extensive and successful taken.

The process in the three differs in important respects and the conditions differ as to (*a*) vacuum pressure; (*b*) sensitiveness; and (*c*) lagging.

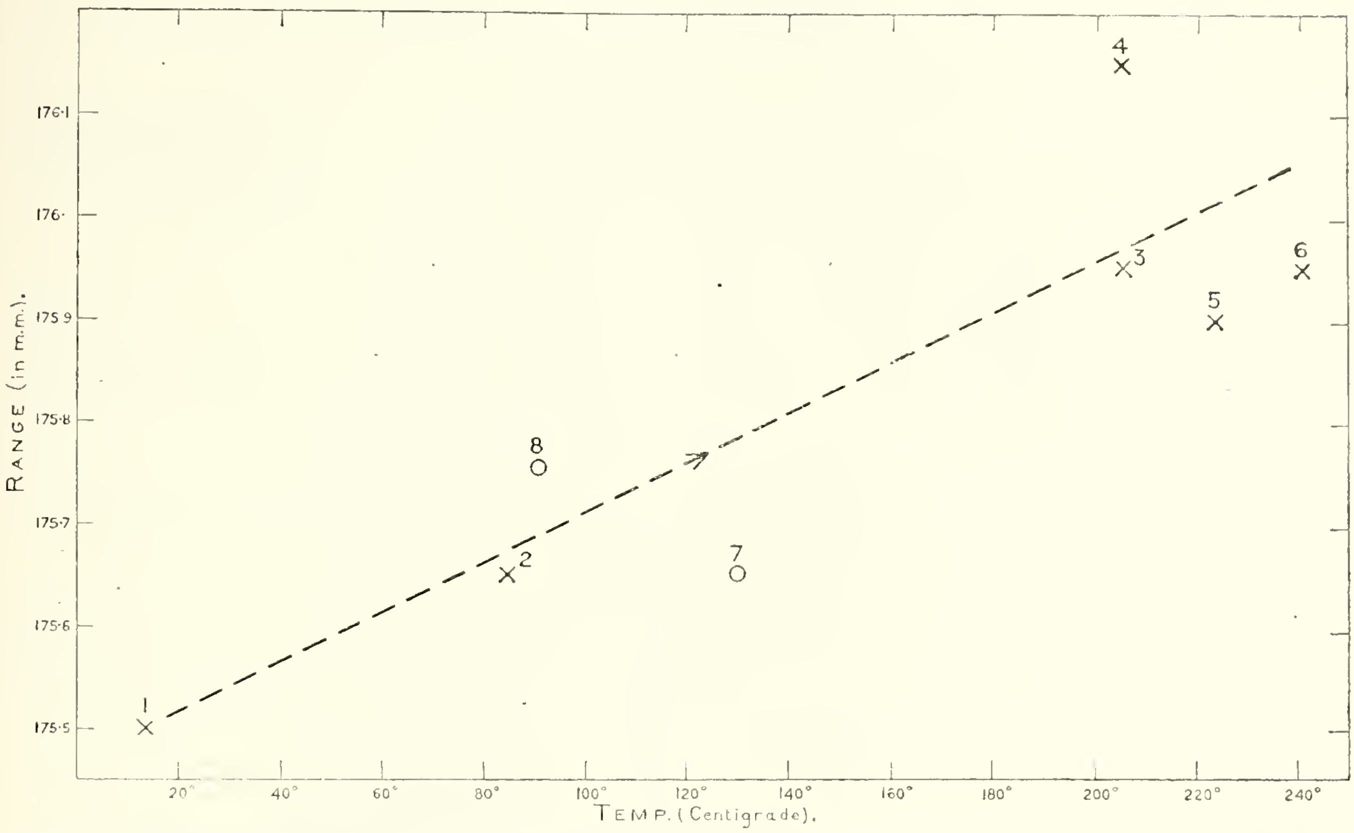

Fig. 14. Graph for Table III. The first three crosses show rising temperatures, the next three are for temperatures high but variable, and the two circles are for falling temperatures.

Out of a total of many scores of experiments eighteen are summarised in Table IV. A great number of experiments have failed because the conditions were unsuitable; for instance, the apparatus may be changed in the attempt to gain accuracy or to apply some test—but this change produces, sometimes, results which are non-cyclic. Or, a new vacuum pressure may be tried, which is unsuitable, the torsion system getting out of control through convection or tremors. In a *few* cases small *negative* temperature effects have been found, but in every case the results have been non-cyclic; for instance, a negative effect when temperature rises may be followed by a positive effect when it falls again. The net result for both rise and fall is found invariably to be a positive effect. But it is non-cyclic and is considered worthless. These negative effects are due to strain and change in position of the parts of the apparatus and have always been removed by proper care.

In Table IV. the high value $+1{\cdot}8 \times 10^{-5}$ and the low value $0{\cdot}5 \times 10^{-5}$ occur and are included in finding the arithmetic mean, which might be considered to be vitiated by their presence. But it is noteworthy that the longest and best experiments give results about $+1{\cdot}2 \times 10^{-5}$ which agree with the mean result and so tend to confirm it.

TABLE IV.—Summarised Results of Several Experiments.

Date.	Range at 15°.	Greatest temperature rise.	Range at highest temperature.	Effect for 1° C.	Comments.
		° C.			
June 23, 1914 . .	57·60	150	57·70	$+1 \cdot 1 \times 10^{-5}$	Chains and cylinders. (See Table I.) Pressure = 1μ.
May 24, 1915 . .	201·9	185	202·5	$+1 \cdot 6 \times 10^{-5}$	Pressure = 2 mm.
,, 26, 1915 . .	209·2	200	209·6	$+0 \cdot 9 \times 10^{-5}$	
July 14, 1915 . .	200·8	135	201·5	$+0 \cdot 9 \times 10^{-5}$	
,, 16, 1915 . .	200·8	180	201·35	$+1 \cdot 4 \times 10^{-5}$	
,, 24, 1915 . .	200·8	150	201·35	$+1 \cdot 8 \times 10^{-5}$	Pressure = 4 mm.
				Let in air to 14 mm. pressure.	
July 27, 1915 . .	200·85	160	201·25	$+1 \cdot 2 \times 10^{-5}$	(See Table II.)
August 4, 1915 . .	200·8	160	201·2	$+1 \cdot 3 \times 10^{-5}$	
,, 5, 1915 . .	196·3	140	196·5	$+0 \cdot 8 \times 10^{-5}$	
,, 8, 1915 . .	193·45	180	193·95	$+1 \cdot 3 \times 10^{-5}$	
,, 10, 1915 . .	193·25	180	193·9	$+1 \cdot 6 \times 10^{-5}$	
,, 12, 1915 . .	175·45	190	175·75	$+0 \cdot 9 \times 10^{-5}$	
,, 18, 1915 . .	175·45	210	173·75	$+0 \cdot 9 \times 10^{-5}$	
,, 19, 1915 . .	175·55	220	176·15	$+1 \cdot 5 \times 10^{-5}$	
				Demagnetise balls.	
August 21, 1915 . .	175·5	200	175·95	$+1 \cdot 3 \times 10^{-5}$	(See Table III.)
,, 22, 1915 . .	199·5	200	199·7	$+0 \cdot 5 \times 10^{-5}$	
,, 24, 1915 . .	201·25	210	201·65	$+1 \cdot 0 \times 10^{-5}$	
,, 25, 1915 . .	190·75	230	191·2	$+1 \cdot 1 \times 10^{-5}$	
				Rotate M, M by 180°.	
August 30, 1915 . .	185·7	150	186·2	$+1 \cdot 7 \times 10^{-5}$	
		Mean effect		$+1 \cdot 2 \times 10^{-5}$	

The readings in columns 2, 4 are in millimetres.

It will be observed that the vacua used vary from 1μ (for chains) down to the low vacuum 14 mm., which proved most satisfactory when tried for spheres, and was used always afterwards.

VII. TESTS APPLIED.

We have now proved that there is a temperature effect which repeats itself with as much consistency as can be expected in a delicate apparatus, where the effect observed is only 0·5 mm. of scale reading. But this effect need not be a gravitation/temperature effect, but may be wholly or in part due to systematic errors in the work. The results are, of course, as the tables show, outside the range of observational error; but the delicate torsion system would be very susceptible to spurious effects, due directly or indirectly to the heat in the large masses, M, M. The steps taken and the tests made to weed out spurious effects will now be indicated.

In § IV. above some likely sources of error have been mentioned, and special precautions were taken against them in designing the apparatus. There are some other troubles possible, mostly mechanical.

(1) The vacuum tube containing the torsion system and spheres, *m*, *m*, hangs from steel springs, and is steadied in every direction by a set of rubber corks separating it from the wooden frame carrying the large masses, M, M. The bottom of the vacuum tube is steadied and can be adjusted by four horizontal set-screws; these screws being set in a metal frame supported from the cement floor of the room. The large masses are separately supported by a stout scaffold. Suppose the position of M, M, relative to the small spheres, *m*, *m*, is ideal, *i.e.*, central and symmetrical. If *m*, *m* were now to move in the plane containing M, M, the sensitiveness of the system would increase—the telescope readings would change; whereas, if they moved in a perpendicular sense the sensitiveness would decrease and telescope readings would change in the contrary sense. It is important, therefore, that during an experiment no movement of either mass system, *e.g.*, due to warping of the framework, should occur. Thus the supports should be rigid and screened from heat.

(2) The rubber corks, mentioned above, must be maintained firmly in place.

(3) It is possible that the masses, M, M, might be hung under strains by the copper wires, and when heating occurs this strain might vary. This possibility was tested (and found non-existent) by turning both masses, M, M, by 180° C. on a vertical axis, as in the last experiment in Table IV.

(4) The centre of mass of the spheres, M, M, might be displaced vertically by expansion as temperature rises. This movement would decrease the couple, due to M, M, on the torsion system, supposing the centres of M and *m* lie exactly in a horizontal line. The masses, M, M, are carried by copper discs (see fig. 9) attached to copper rods which pass through holes in the masses. The radius of each mass is 10 cm. Thus, when temperature rises 200° C. we have the centre of mass rising $2 \cdot 8 \times 200\mu = 560\mu$, due to expansion of the lead; and falling $3 \cdot 2 \times 200\mu = 640\mu$, due to expansion of copper (the coefficients of the two materials being 28×10^{-6} and 16×10^{-6} respectively). The net fall in the centre of mass would then be 80μ. Now the large masses, M, M, are 150 mm. from the small ones, *m*, *m*, and the small cosine error resulting from the vertical movement 80μ, will be found negligible. If, however, due to error in setting, M and *m* are not on a horizontal level, but that the former be 5 mm. above its ideal position (an error of setting which is most unlikely) we should then find that the fall in the lead would give an effect of order 10^{-5}, which is negligible compared with our effect of 2×10^{-3}.

(5) If the temperature of the quartz torsion fibre rises during the experiment, its rigidity will change and the telescope readings will be affected.

In Table III. the indicated temperature change in column 9 is 0·2° C. from beginning to end of the experiment. There is reason to think that this change is almost entirely due to heat getting into the thermometer above the water cooler where it would not affect either the torsion fibre or the lower part of the suspension. But suppose for present purposes we allow a temperature rise of 0·3° C. Fuzed quartz has temperature coefficient -1×10^{-4}; thus the fibre would be *stiffened* by $0{\cdot}3 \times 10^{-4}$. Our temperature effect is 20×10^{-4}. So we see that this error may be considered negligible numerically and it acts in *the wrong direction*.

The following list comprises the sources of error mentioned here and in § IV. The first four are due to heat entering the vacuum tube, the last six to the effects of heat on the masses, M, M, and other parts external to the vacuum :—

1. (Temperature change in fibre).
2. (Convection).
3. Radiometric pressure.
4. Radiation pressure.
5. (Electrostatic forces).
6. Magnetic forces.
7. (Movement of base of vacuum tube).
8. (Movement of top of vacuum tube).
9. (Rotation of M, M).
10. (Rise or fall of M, M, due to expansion.)

The numbers of this list enclosed in brackets have already been dealt with and may be considered to have been eliminated by precautions already indicated. Nos. 3 and 4 may be grouped together as they will invariably act in conjunction ; thus we have two errors left to deal with.

No. 6.—The susceptibility of purest lead is -1×10^{-6}; that of iron for weak (earth) fields is, say 10. Thus a trace of iron, 1 part in 1,000,000, would mask any magnetic effect of the lead. Commercial lead has traces of iron varying from 1/300,000 to 1/5000 according to the source.* Suppose the lead used for M, M is of the worst commercial quality. The spheres, M, M, each weigh 50 kilos. so that a rod of iron 20 cm. long weighing 10 gr. should have a greater magnetic influence than the presumed iron impurity in the lead. I placed iron rods of this mass in each sphere, and found the spheres, thus loaded, acted appreciably in the same way, as regards temperature effect, as when unloaded. Thus the temperature effect on the susceptibility is negligible.

We have so far considered only the large spheres, M, M ; but it is evident that if the small spheres, m, m, are quiteun magnetised, the susceptibility of M, M would be immaterial. Separate tests were therefore made on the magnetism of m, m, and these

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* See THORPE's 'Dictionary of Applied Chemistry.'

tests may be considered crucial. Curiously, it was found that though these were the purest silver obtainable from Messrs. Johnson, Matthey and Co., they were both in slight degree permanently magnetised. This is in itself an interesting fact. The torsion system used here is, in this case, a most sensitive magnetometer and when a N. pole of a bar magnet was brought outside the vacuum, slightly above one silver sphere, it repelled it, the corresponding scale reading being 4 mm.; whereas when the N. pole was below, there was a like attraction. This permanent magnetism was removed with some difficulty by the passage of a current through a coil round the vacuum tube, until at last the scale reading was reduced to the small amount of 0·2 mm. for each sphere. Thus the permanent magnetism was reduced to 1/20th of its former amount. Several days later the spheres, m, m, were again tested and were found to remain demagnetised. Probably the permanent magnetism was originally produced when the heating coils round the vacuum tube were excited during production of the vacuum. (See § VI., paragraph 9.)

The above demagnetisation of m, m occurred on date 20th August, 1915, after which, as is seen from Table IV., several full experiments were performed yielding results similar to those found before demagnetisation. From this one may deduce that magnetisation does not influence our gravitation/temperature effect.

Nos. 3 and 4.—These are taken last, their effect being the most difficult of all errors to dissect out from the net result. No calculation can be made of the forces set up due to their action since we do not know the amount or distribution of the supposed irregular heating on the inner face of the vacuum tube. The apparatus was designed and fitted up to avoid these errors to the utmost. There are a great number of layers of cotton wool, paper and flannel both inside and outside the helical water-jackets. Also extra screens were in some cases arranged to keep heat from the vacuum tube. The water passing through the water-jacket was steady in temperature for long intervals; any small rises in temperature due to the source would, in a long series of experiments, pair off against similar falls. The water flowed at a great rate, say, 3 to 6 litres/minute. It is hard to believe that any heat from the thickly-lagged lead spheres could penetrate the water-jacket and cotton wool under these conditions. But one can never be sure, without special tests, that heat will not find some joint or weak spot in the lagging and so reach the vacuum tube somewhere. If the inside of the vacuum tube were warmed irregularly we might have radiometric pressure effects; but even then one would expect no change in the range (see Table II., column 7), but rather a removal of the same range up or down the scale. The special tests applied were:—

(*a*) The tap water was heated before entering the helix and it was found that a change in telescope readings occurred at first, but that when the temperature became steady, though raised, the readings became normal.

(*b*) More and yet more wrappings were put over the helixes, so that weak places, if any existed, would be covered up. It will be observed that the numbers in column 2,

Table IV., vary for spheres from 209 to 175. This is due to the fact that as more wrappings are used, the masses, M, M, can be swung through less angle; hence the range is reduced. Thus we have some eight degrees of wrapping indicated in the above table.

(*c*) The outer layer of cotton wool was covered with tin-foil, and several experiments were performed in which the parts of the helix coverings, near the hot spheres, M, M, were sprayed with tap water every two minutes. The experiments on dates 18th August, 1915, and 19th August, 1915, in Table IV., were conducted thus. In this way the helix coverings remain cool always.

Seeing then that similar results are obtained under all these varying conditions as to temperature and conductibility of the surface of the central tube containing the vacuum, it seems permissible to state that the effect observed is not attributable to radiometric pressure or other forces due to the entrance of heat through the walls of the vacuum tube. A further reason why radiometric pressure should be counted out is that like effects have been found for vacuum pressures varying from 2 mm. to 14 mm., so that the corresponding radiometric pressures, if existing, would drop in the ratio about 5 to 1. Yet Table IV. shows no material difference in the results throughout these changes.

In like manner, none of the other possible errors, scheduled above, seem capable of giving the observed temperature effect. So, unless some other error has been overlooked or some agency, at present unknown, comes into play, we must conclude that, at least for lead there is a temperature effect of gravitation. The plotted results in figs. 13 and 14 do not lie on smooth curves. But it will be observed that the scale of ordinates is very open.

Still, provisionally, the foregoing numerical results have been worked out on the basis of a linear relation,

$$f = \mathrm{G}\,(1+\alpha\theta)\,\mathrm{M}m/d^2$$

Where α is a temperature coefficient of amount

$$+\,1\cdot2\times10^{-5} \text{ per } 1^\circ \text{ C.}$$

It will be observed that my results overlap the weight experiments of POYNTING and PHILLIPS (§ I., 3) for range of temperature 20° C. to 100° C. I cannot speak with any certainty as to the effect in my apparatus for this small range. If the effect be linear, the scale movement would be under 0·2 mm., *i.e.*, too small an amount to be sure about. But the effect may increase much faster than temperature, in which case one could not expect to observe any result for a range 20° C. to 100° C. It must also be remembered that (as stated in § II.) these experiments are not strictly comparable with the weight experiments, and so, for various reasons, we see that the two results, which appear to differ considerably, do not necessarily clash. No other investigations on the subject have yet been made.

VIII. Conclusion.

1. *Technical Summary and Suggestions.*—As the experimental work has been long and troublesome, it may not be out of place here to summarise the more important technical difficulties met and overcome. To perform this research it has been found necessary :—

(1) To obtain a sealing material for making joints between a quartz or metal fibre and any metal including aluminium, so that the joints should stand a temperature of 160° C. and considerable load. No wax would do, and no ordinary solder with flux, but the alloy of 88 Zn/12Sn acted perfectly.* In the final experiments a quartz fibre, 15μ diam., was attached thus to brass above and silver below, the load being seven gm. (which is little short of the breaking load). This stood for seven months though subjected to lateral shock and long-continued temperature of 130° C.

(2) To realise a system of a delicate torsion balance in a high vacuum, provided with an optically true window. After long trial a wax of high melting point was found for fastening the two windows, but, of course, no wax is vapour-free when heated. Yet heating is essential for the production of high vacua. The joints containing the wax had, therefore, to be carefully treated in the preparation of the vacuum.

(3) To test the quartz fibres. These fibres, while splendid in torsional qualities, are most uncertain as to-tensional strength. Systematic testing was therefore always adopted.

(4) To damp out tremors in a delicate torsion system in a high vacuum while leaving the main (torsional) oscillation free. None of the many known methods of damping is here permissible. But if a chain be suspended from the torsion beam, its links provide rolling friction at every tremor and the damping is excellent. Without this chain method, such measurements as these with high vacua would appear to be impossible under the conditions of the experiment.

(5) To guard a delicate torsion system from external vibrations so as to make it useable even in a large city. The apparatus, heavily loaded with lead, was suspended by steel springs and steadied on all sides by rubber bungs. The vault in which the experiments were made is immediately under a workshop. Yet with this system, continuous readings could be taken even when the lathes and anvil were in use. Again, the movement of the heavy masses, M, M (total weight 100 kilos.) throughout the experiments, caused no trouble.

No doubt these investigations will be repeated and extended. In the general design I cannot suggest any improvement. The final form I used, which in type resembles that originated by Prof. C. V. Boys, worked excellently and was sensitive. I have long felt that the greatest defect, or rather weak spot, in the apparatus lies in

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* See Shaw, "Sealing Metals," 'Proc. Phys. Soc.,' January, 1912.

the window, which necessitates a break in the water-jacket system to allow light to enter the window and return to the telescope; and though an elaborate system of water helix and lagging is provided in the window region (not fully shown in any figure) one feels that here there is a joint in the armour through which heat may enter. The ideal vacuum tube would have no front window on the wall of the tube. The light from the scale would enter the top window and pass by two totally reflecting prisms to and from the mirror back to the telescope. The optical difficulty in realising this plan would no doubt be great, but if it were possible we should have the great advantage of a *continuous* water-jacket, without joints, from end to end of the vacuum tube.

Suppose, however, the ideal arrangement could not be made to work, one seems to have only one alternative if the window defect, above indicated, is to be minimised. This alternative is to reduce the bore of the vacuum tube to, say, 36 mm., and the beam to, say, 25 mm. The window would be reduced proportionally and it might then be possible to have a continuous water-jacket with a small slit opening at the window. In reducing the beam as just suggested we should have the further advantage of reducing the period of oscillation to one half. Sensitiveness would be slightly lessened, but spurious heat effects, if any, would be greatly reduced.

2. *General Summary*.—I. It has been found possible :—(*a*) to obtain consistent cyclic readings in a gravitational experiment of the Cavendish type, even though the large masses are maintained for hours above 200° C., while the small masses remain at ordinary temperature; (*b*) to carry on this investigation in the centre of a city at any time by day or by night, in spite of the attendant tremors and the special disadvantage of having the torsion balance in a vacuum.

II. The conclusion reached is that there is a temperature effect of gravitation. *When one large mass attracts a small one, the gravitative force between them increases by about 1/500 as temperature of the large mass rises from, say, 15° C. to 215° C.* At present the result is provisionally stated as being $+1{\cdot}2 \times 10^{-5}$ per 1° C.; but the readings are not steady enough to justify the statement that there is a *linear* relation for G/θ. It seems possible that time may be a factor in the effect; but the net result has not been shaken by a long series of tests.

III. The above result, though new, is not entirely unsupported by other experiments, for previous gravitation experiments give indirect evidence of a positive temperature coefficient. The weight experiments of POYNTING and PHILLIPS, which yielded negative results, are not strictly comparable with mine.

IV. As a bye-product of these experiments, it was found that silver balls of the highest purity, after being heated to 130° C. and placed in a strong magnetic field, were permanently, though weakly, magnetised, and that the coercivity was considerable. This is probably due to residual iron, see § VII. 6.

V. Several technical troubles overcome during the research are summarised above.

For much general assistance from friends and colleagues, during the progress of this work, I gladly acknowledge my indebtedness. All the readings have been taken by myself; but on many occasions during the preparation of the apparatus, I have received most willing aid in various ways. To the many who have thus assisted me in accomplishing the present work I wish to record my thanks. I am also much indebted to Messrs. Baird and Tatlock, Hatton Garden, E.C., for great help in glass blowing.

This investigation could not have started nor continued without considerable expenditure on apparatus. At the kind suggestion of Prof. W. H. HEATON, the Council of University College, Nottingham, made a generous grant at the outset, eight years ago; while Prof. E. H. BARTON has greatly helped by his unquestioning supply of material.

Finally, I wish to acknowledge my obligation to Prof. C. V. BOYS and the late Prof. J. H. POYNTING for kind advice at the commencement of the work.

[*Notes added April 25, 1916.*—Since the reading of this paper two possible sources of error, in addition to those in the table above (p. 386), have been suggested:—

I. As temperature rises, the air surrounding the spheres, M, M, will decrease in density, so that the total gravitative pull felt by the torsion system, due to the external system, will be reduced.

Let ρ be the mean density of lead and lagging and let ρ' be the mean air density. The effective large mass is really $M(1-\rho'/\rho)$. Both lead and air expand, and we must calculate (*a*) the mass of cold air displaced by the expanding lead; (*b*) the mass of air expelled from the field by expansion of air shells round the lead.

Under the first head. Let the sphere have radius r and expand to $(r+\delta r)$, with rise of temperature $\theta°$. The mass of the air shell displaced is, calling β its coefficient of expansion,

$$\begin{aligned} &4\pi r^2 . (\delta r) . \rho' \\ &= 4\pi r^2 (r\beta\theta)\rho' \\ &= 1/14 \text{ gm., approximately.} \end{aligned}$$

But M = 50,000 gms., so the proportionate change in the attraction due to this cause would be 1/700,000. This is negligible.

Under the second head. Suppose, as an extreme case, a shell of cold air equal in volume to the lead were removed from the field by expansion; the mass of this would be 1/9000 of the mass M. This also is negligible, since the temperature effect observed is 1/500.

II. With the high temperature of the lead spheres (250° C.) considerable convection currents would be set up round them, even when lagged.

In the region where the spheres are close to the tube, the air velocity might be very much larger than on the outer regions; and, as a consequence, difference of pressure would be called into play, pushing the suspended spheres towards the tube and therefore increasing the actual attraction on the suspended small balls.

Let α be the temperature effect as found in this research, and let dr be the actual displacement accounting for it, on the above supposition, we have

$$G\,.\,\frac{Mm}{r^2}\,.\,\alpha = 2G\,.\,\frac{Mm}{r^3}\,dr,$$

hence

$$dr = \alpha r/2.$$

As

$$r = 15 \text{ cm.,} \qquad \alpha = 0{\cdot}002,$$

we have

$$dr = 0{\cdot}015 \text{ cm.}$$

If the mass M have weight W, and hang at distance l from the supports, the force required to produce this movement (dr) is

$$W\,.\,dr/l = 5{\cdot}5 \text{ gm. weight.}$$

In discussing this hypothesis of greater convection on the inner side of the mass M we should notice that the vacuum tube is surrounded by a water screen at about 11° C., so that one would expect the inner side of the sphere to be colder, not hotter, than elsewhere, and the push on the sphere due to convection differences would be *outwards, not inwards.*

Suppose, however, that through some cause there is greater convection on the inner side of M. By applying BERNOULLI'S theorem we can calculate what velocity is required to give the calculated push of 5·5 gm. weight.

Let v_0, v be convection velocities on the outer and inner sides of the sphere ; and let p_0, p be the corresponding pressures ; and let d be the air density. We have

$$\frac{v^2-v_0^2}{2} = \frac{p_0-p}{d}\,.$$

The effective area (*i.e.*, the total resolved area of the sphere on which the pressure difference, p_0-p, acts horizontally) would be not more than 75 cm². Then taking $v_0 = 0$ we find $v = 380$ cm./sec. If, however, we take $v_0 = 100$ cm./sec. we find $v = 360$ cm./sec. It is fair to assume that v_0 lies between 0 and 100 cm./sec.

Thus the upward velocity of a broad column of air on the inner side of the sphere would have to be some 370 cm./sec. to account for the observed effect. This velocity is enormous. Even if the large value of 37 cm./sec. were assumed the error introduced would be only 1 per cent.

In a recent paper by H. A. WILSON* we find it stated that the velocity of a bunsen flame is only 300 cm./sec. So, even supposing there were proved to be excess convection on the inner side, we have no reason to think that it would introduce a calculable effect.]

* 'Phil. Trans.,' A, 1915, vol. 216, p. 71.

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SERIES A, VOL. 216. Pp. 393–427

THE COMBINING VOLUMES OF HYDROGEN AND OXYGEN.

BY

F. P. BURT, D.Sc.,

AND

E. C. EDGAR, D.Sc.,

SENIOR LECTURERS IN CHEMISTRY IN THE UNIVERSITY OF MANCHESTER.

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VIII. *The Combining Volumes of Hydrogen and Oxygen.*

By F. P. Burt, *D.Sc.*, *and* E. C. Edgar, *D.Sc.*,
Senior Lecturers in Chemistry in the University of Manchester.

Communicated by Prof. H. B. Dixon, *F.R.S.*

Received December 2, 1915,—Read February 24, 1916.

The measurement of the combining weights of hydrogen and oxygen has been the subject of so many researches of a high order of excellence that any fresh investigation of this fundamental constant must be submitted with considerable diffidence. Nevertheless, it must be noted that the results obtained by various observers differ appreciably. According to Clarke(¹), the values obtained by Morley and Noyes, by reason of the accuracy of their methods and the close concordance of the individual determinations, outweigh the results of all other investigators. The atomic weight of oxygen being 16, that of hydrogen, according to Morley(²), is 1·00762, and according to Noyes(³), 1·00787. (Clarke, on Noyes' data, prefers the value 1·00783.) It is, further, a significant fact that the arithmetic mean of all determinations discussed by Clarke, lies between these two values, which differ by 1 part in 4000. Both values are based on the gravimetric synthesis of water and are independent of a knowledge of the densities of the gases.

A physico-chemical method of determining the relative molecular weights depends on the knowledge of the ratio of the densities, together with that of the combining volumes.

The present uncertainty in the values of these two constants is probably greater in the case of the combining volumes. The classical researches of Morley have established the densities of hydrogen and oxygen within very narrow limits, and, according to Clarke, writing in 1910, Morley's value for the ratio is to be preferred to any other. There are now, however, good reasons for believing the density of oxygen to be slightly greater than Morley's value, perhaps by 1 part in 28,000, though no subsequent work has advanced a more probable alternative to his value for hydrogen. Comparatively few investigations on the combining volumes have been made; of these, the two most important are due to Scott and Morley respectively. The historic researches of Scott(⁴) led to a value of 2·00245—this value being increased by him to 2·00285, when the necessary corrections (in calculating from room temperature to 0° C.) were made for the difference in the temperature coefficients of

[Published June 5, 1916.

the two gases. MORLEY(5), by a less direct method, arrived at the value 2·00269. (CLARKE, on MORLEY'S data, gives 2·00274.) A few experiments by LEDUC(6) yielded a considerably higher figure, 2·0037, and later, 2·0034, whilst RAYLEIGH(7), from compressibility measurements, obtained the slightly lower value 2·0026.

The agreement between the values of SCOTT and MORLEY is exceedingly close, but in view of the uncertainty of some necessary corrections in MORLEY'S work, there is some excuse for a further series of determinations in which the gases, before combination, are measured at 0° C. and 760 mm. pressure, that is to say, under the conditions of the density determinations. By adopting this procedure any errors due to uncertainty in the temperature and pressure coefficients are eliminated. This is the object of the present research.

The experience of previous workers shows that the chief difficulty presented by the problem is the preparation of the two gases in a state of purity. To ensure the absence of traces of foreign gases, in particular chemically inert gases such as nitrogen or paraffin hydro-carbons which cannot readily be removed by chemical re-agents, the most stringent precautions must be taken. In selecting a method for preparing a gas it is less important to secure a high initial state of purity than to avoid the introduction of substances that are afterwards difficult to separate; the presence of a trace of nitrogen may be much more troublesome than a considerable quantity of carbon dioxide. Treatment of gases by strongly heated solids is often unsatisfactory, because, although a particular impurity may be eliminated, some other impurity may be acquired.

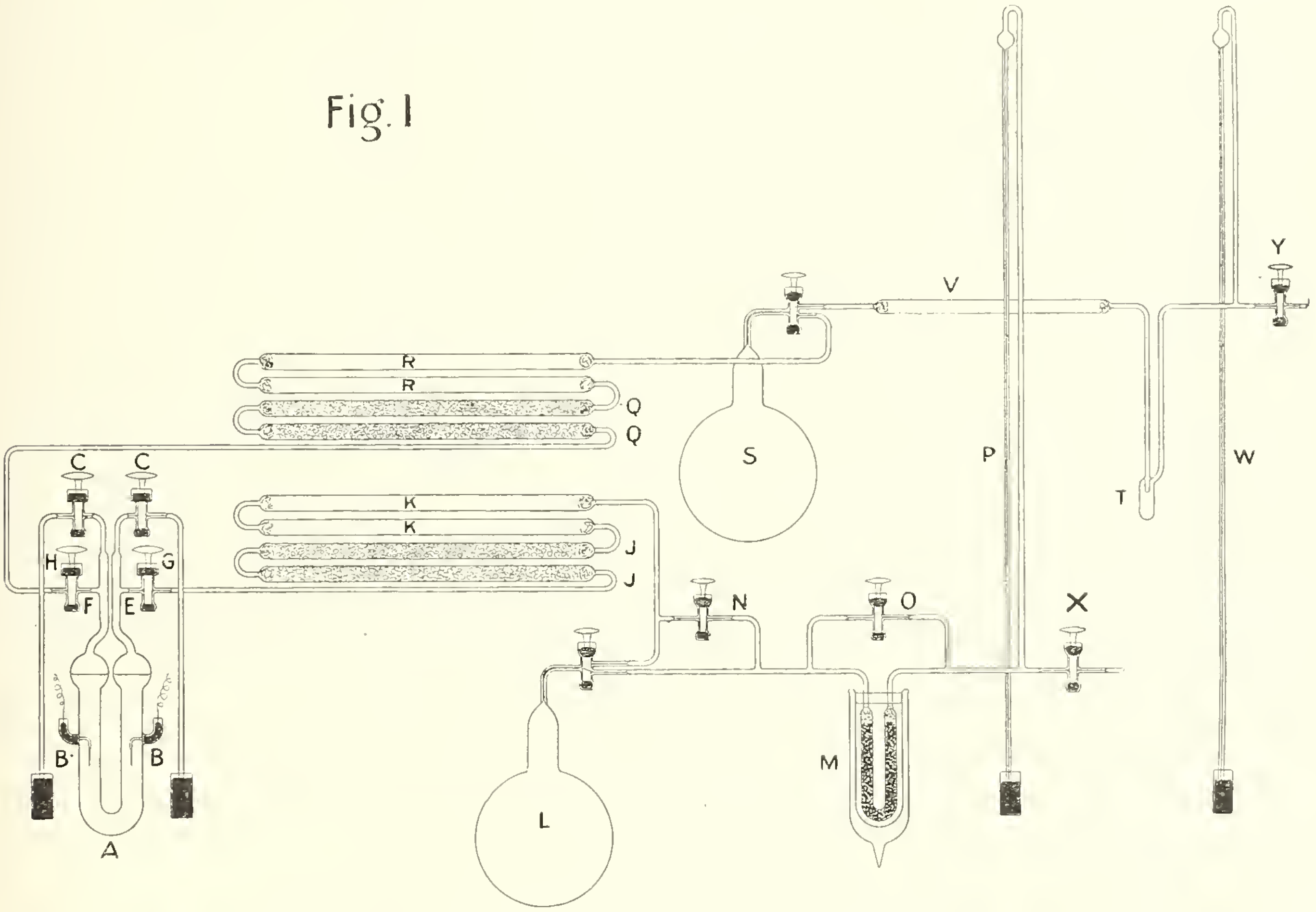
In this investigation we have relied on physical rather than chemical methods for the ultimate purification of the gases. The case of hydrogen is peculiar in that it cannot conveniently be liquefied, but advantage may be taken of this very fact to separate impurities that are more readily condensible.

We began this investigation in July, 1911, and completed the experimental work in July, 1915. The apparatus was set up in an underground cellar below the Schunck Laboratory, and this room was reserved exclusively for our use.

Preparation of Hydrogen.

The work of H. B. BAKER has shown that very pure gas is obtained by the electrolysis of an aqueous solution of barium hydroxide, and this is the method we have adopted throughout for generating hydrogen. The electrolysis was carried out in a U-tube constructed of boro-silicate glass (fig. 1, A), fitted with electrodes of stout platinum foil, about 27 mm. square. The platinum wire seals at B and B were mercury cupped. The two limbs of the U-tube were sealed to the soda glass connecting tubes by means of a glass of intermediate composition. The extension of each limb was bent over to form a short manometer which dipped into mercury; these manometers could be closed by the taps, C, C. T-pieces at E and F conducted the gases through the taps, G and H, to the drying trains. Before one of the manometers was sealed on, a hot saturated solution of Kahlbaum's barium hydroxide, which had been four times re-crystallised by us, was filtered through glass wool into the U-tube; the manometer was immediately sealed on, and electrolysis started, and then the vessel was exhausted by a water pump until the solution boiled. Finally, both hydrogen and oxygen were allowed to run to waste through the gauges for a considerable time, so as to complete the elimination of air. A large proportion of the hydroxide crystallised out on cooling, and partially dissolved again when the temperature rose owing to passage of the current. No partition or diaphragm was employed in the U-tube, as the subsequent treatment of both hydrogen and oxygen was designed to remove traces of the other gas. A current of about 1·5 amperes was used for electrolysis, and the solution was not allowed to get very hot.

Fig. I



Purification of Hydrogen: First Method.

The hydrogen from the electrolysis vessel, after passing through two drying tubes filled with calcium chloride, J, J, and two filled with Merck's phosphoric oxide, K, K, entered the $2\frac{1}{2}$-litre storage bulb, L, which was fitted with a 3-way tap. This bulb, after exhaustion by a water pump and a mercury pump, had had the last traces of air removed by four hours' exposure to charcoal cooled in liquid air. The storage bulb was connected to the U-tube, M, containing charcoal. This tube had been prepared in the following way: 11·5 gr. of charcoal, made from cocoa-nut shell, were introduced into the tube in fragments the size of a pea. The tube was exhausted by a water pump, and then heated in a glycerine bath to a temperature of 240° C. Dry hydrogen was next admitted and then pumped out again, and this operation was repeated several times. Finally, the tube was exhausted at 240° C. and sealed off. When cold, dry air was admitted, and the tube was immediately sealed to its connections on the apparatus. The observations of DEWAR (8) and, more recently, of CLAUDE (9), indicate that, in the absence of helium and neon, exposure of hydrogen to charcoal at liquid air temperatures should prove a very efficient method of removing other gases. Hydrogen itself is absorbed to a considerable extent. According to the measurements of CLAUDE, 100 gr. of charcoal, cooled to −195°·5 C., can take up about 20 c.c. of hydrogen before the pressure reaches a tenth of a millimeter of mercury. Five litres of nitrogen are required to produce a similar pressure, whilst oxygen is still more readily absorbed. When cooled in liquid air and put in connection with the 2½-litre storage bulb, containing hydrogen at atmospheric pressure, the 11·5 gr. of charcoal in our U-tube reduced the pressure to about half an atmosphere. By closing the storage-bulb tap and admitting hydrogen from the electrolysis vessel and drying train through the cross-tube, N, the charcoal vessel was rapidly filled to atmospheric pressure. Electrolysis was then continued until sufficient hydrogen had been passed over the cooled charcoal to charge the measuring vessel. The liquid air vessel was then removed and part of the gas from the charcoal was allowed to return to the storage bulb. The later fractions were removed by the mercury pump, the train being exhausted at the same time. In this way impurities which had been retained by the charcoal were prevented from accumulating in the system. A cross-piece, O, carrying a tap connected the two limbs of the U-tube so that the train could be pumped out by another path in addition to that through the charcoal. A mercury gauge, P, recorded the pressure of gas in the system.

Purification of Hydrogen: Second Method.

The gas was dried, as before, over calcium chloride and phosphoric oxide, but, in some series of determinations, passed first through a tube containing palladium black to remove oxygen. After leaving the drying train the hydrogen was made to pass through the walls of a heated palladium tube (fig. 2, A). This tube, 10 cm. long, 1 cm. in external diameter, and having a wall thickness of about 0·6 mm., was welded to 3 cm. of platinum tube of similar dimensions. The platinum was sealed to a glass tube, B, which, in its turn, was fused as an inserted join into a wider tube, C, connected at its other end with the drying train. The wide tube thus formed a cul-de-sac into which the blind end of the palladium tube projected backwards. A short cylinder of quartz was slipped over the palladium tube and wound with a spiral of platinum wire, the terminals of which made contact with stout platinum hooks sealed through the glass of the outer tube. By passing a current through the wire the palladium could be heated to any desired temperature.

The junction between the thick platinum tube and the glass was an excellent piece of workmanship carried out by Baumbach, the University glass-blower; it was quite free from air-bubbles and absolutely gas-tight. For a year and a half it has been constantly heated and cooled, and no sign of a crack has ever appeared.

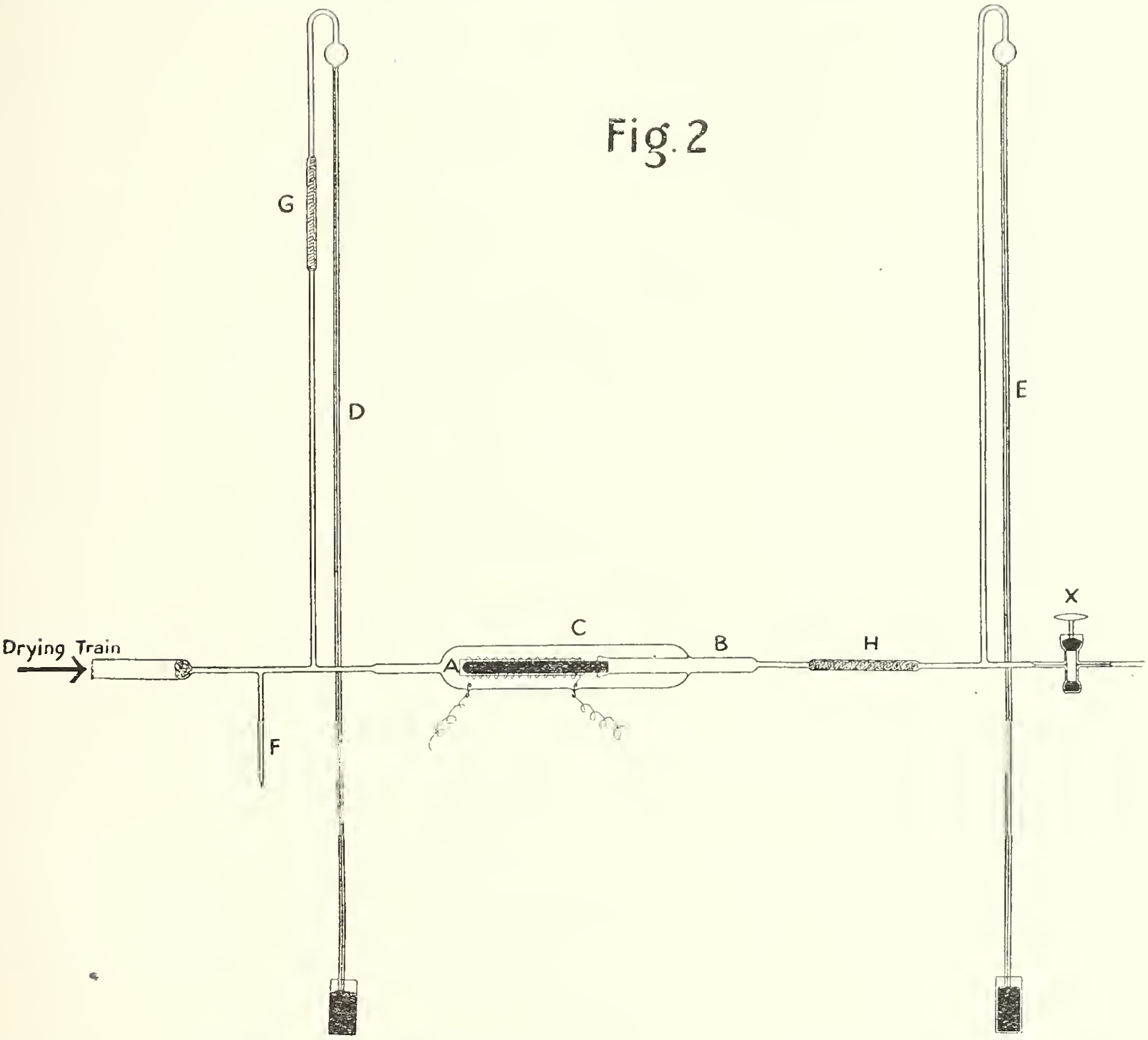


Fig. 2

The three palladium tubes used in this work were obtained from Messrs. Johnson and Matthey. The first tube was made from forged sponge; the second and third from fused metal. The third tube (the one figured in the diagram) contained 0·5 per cent. platinum and a trace of rhodium which were deliberately left in with the idea of increasing its mechanical rigidity. The weight of palladium in the second and third tubes was about 26 gr., but the third tube, the dimensions of which have already been stated, was made about twice the length and half the wall-thickness of the second. The tube prepared from forged sponge showed a marked tendency to become crystalline and develop cracks, and for this reason was soon discarded. We have to express our indebtedness to Messrs. Johnson and Matthey for the great trouble they took in preparing tubes that would satisfy our requirements.

Before admitting hydrogen it was necessary to make certain that both the palladium itself and the glass-platinum junction were perfectly gas-tight. The palladium tube was evacuated by means of the mercury pump while the drying train was left full of air at atmospheric pressure, and the apparatus was allowed to stand overnight. In the morning the mercury gauges at D and E indicated no alteration in pressure on the two sides of the system, nor could any gas be obtained from the pump. After the palladium tube had been strongly heated, the vacuum still held. The drying train was now exhausted at the T-piece, F, and the palladium heated to a much higher temperature than was ever afterwards reached in the actual determinations. The train was then washed out with hydrogen, and this operation was repeated till all air was removed, when the T-piece, F, was sealed off.

Sometimes difficulty was experienced in "activating" the palladium. This could be effected by heating *in vacuo*, by heating in hydrogen, or, perhaps most surely, by heating in air. Once activated, the palladium remained in this condition throughout our experiments. The superficial film of oxide formed by heating in air disappeared when hydrogen was admitted. All the tubes used by us were permeable to hydrogen even in the cold, but the rate of passage of the gas was exceedingly slow. No movement of mercury in the gauges could be detected by eye, and equilibrium was only established after ten or twelve hours when the initial difference of pressure on the two sides of the system was as great as half an atmosphere.

In order to obtain hydrogen in the requisite quantities, the following procedure was adopted:—Electrolysis was continued until the pressure of hydrogen in the palladium was nearly atmospheric; if the palladium was heated at once, almost all the gas was evolved from the surface at which it had entered; if twenty-four hours were allowed to elapse before heating, hydrogen was evolved freely at both sides of the system. By keeping the metal at a temperature of 100° C. during charging, the process of diffusion was greatly accelerated. The required quantity of gas was obtained by heating to a temperature of 180° C.; after the expulsion of about 300 c.c., the metal was at once recharged at a lower temperature.

When the palladium was allowed to cool, the mercury in the gauge, E, rose rapidly to atmospheric height, and then fell very slowly till its level was the same as in the gauge, D. The life of the tube was certainly prolonged by keeping the palladium fully charged with hydrogen, and by using only a gentle heat to expel the gas. In order to obviate waste of gas through the gauge, D, a $2\frac{1}{2}$-litre storage bulb was attached to the train immediately after the electrolysis vessel. The palladium was protected from the action of mercury vapour by plugs of fine gold wire at G and H.

The last palladium tube used in this work was set up in January, 1914. During the following seventeen months, 20 to 30 litres of hydrogen passed through it. On June 1st, 1915, it was deprived of hydrogen as completely as possible by heating and pumping off the gas. Air was then admitted to the drying train by the T-piece, F, and the apparatus was left over a week-end. When examined again not a trace of gas could be found in the pump. The air in the train was next replaced by nitrogen and the palladium was heated for five and a half hours continuously by the maximum current used in the actual determinations, with the same negative result. Finally, after the apparatus had remained for six weeks with nitrogen at atmospheric pressure outside the tube, the interior was still vacuous.

Preparation and Purification of Oxygen: First Method.

Oxygen was first prepared by electrolysis of barium hydroxide solution in the U-tube already described. The gas, after being dried over calcium chloride (fig. 1, Q, Q), and phosphoric oxide, R, R, entered the 2½-litre storage bulb, S, till this was filled to atmospheric pressure. The storage bulb had been previously exhausted in the same manner as the hydrogen bulb. On immersing the small fractionating tube, T, in freshly made liquid air, more than a litre of oxygen could be withdrawn from the storage bulb over the phosphoric oxide in the tube, V, and condensed as a liquid. If desired, the storage bulb could then be re-charged by continuing the electrolysis, and a further quantity of gas could be condensed in T. About one-third of the liquid oxygen was allowed to escape into the air through the gauge, W, so as to eliminate traces of hydrogen or other low-boiling impurities. The next fraction was taken for the determination. A portion of the residue was returned to the storage bulb and the last fractions were boiled away into the air. The gas finally remaining in the apparatus was removed by the pump.

Second Method.

Oxygen as prepared above might possibly contain traces of hydrogen, though the solubility of this gas in boiling oxygen is certainly very small.

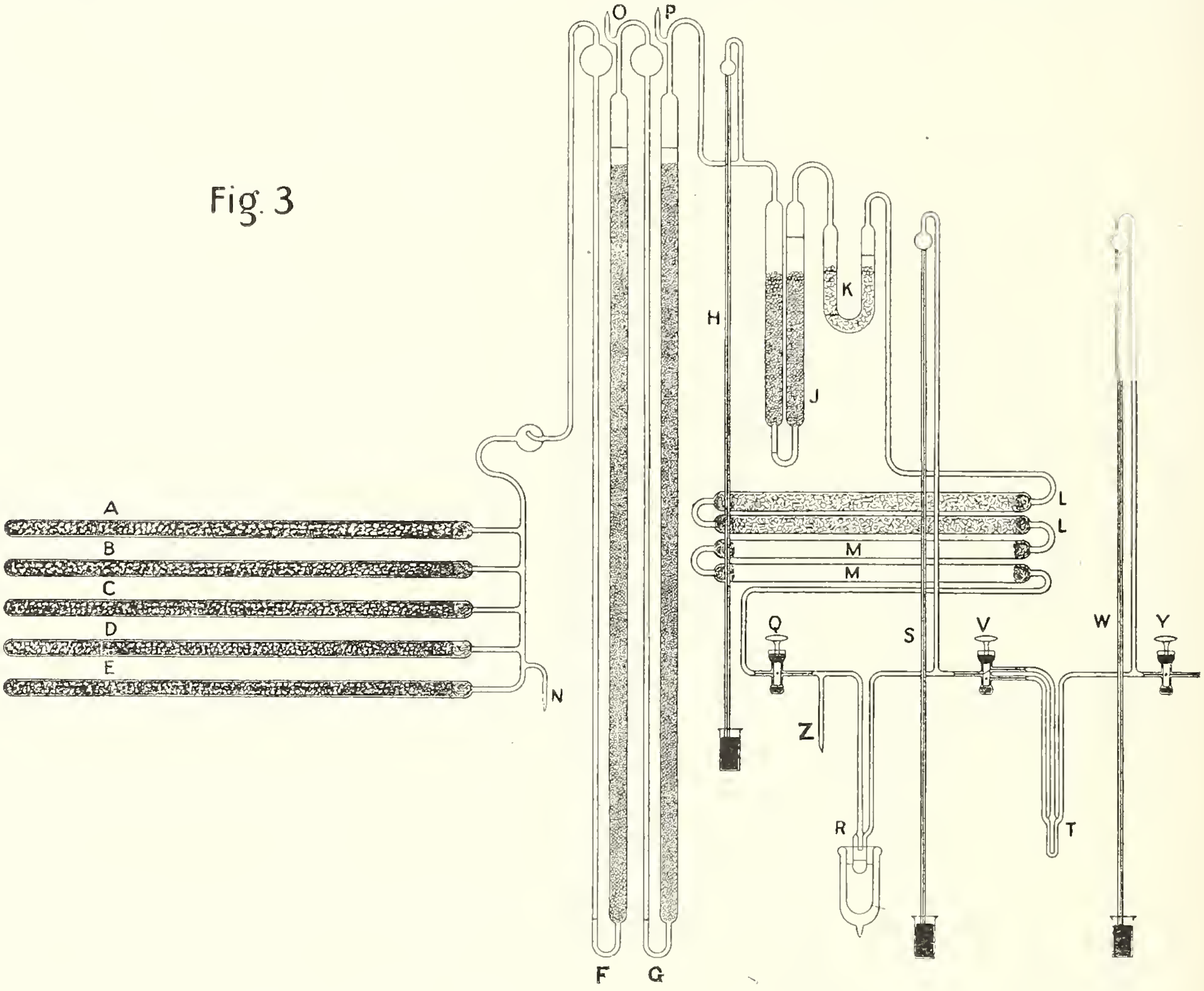
It was deemed advisable, therefore, to make oxygen by some other method which could not conceivably yield hydrogen as an impurity. Gas generated by heating potassium permanganate should fulfil this condition, and was consequently employed to check the results obtained with electrolytic oxygen.

Each of the four tubes, A, B, C, D (fig. 3), was charged with 250 gr. of finely powdered crystals of "pure" potassium permanganate in a dust-free atmosphere. The permanganate in the fifth tube, E, was three times re-crystallised from boiling water. The final crystallisation and subsequent drying were carried out in the decomposition tube itself. We may mention here that there was no difference in the results whether oxygen was made by heating this tube or one of the other four. The mouths of the five tubes were plugged with carefully cleaned glass wool.

From the generating tubes the oxygen passed through a series of three washing towers filled with glass beads.

The first tower, F, contained a moderately strong solution of caustic potash; the second, G, a saturated solution of barium hydroxide. The column of liquid in each tower was over a metre in height. Between the barium hydroxide tower and the next washing vessel a manometer, H, was attached to the train. The short tower, J, contained a stronger solution of potash, and the U-tube, K, a very concentrated potash solution on pumice that had previously been heated in a stream of oxygen. From the U-tube, K, the gas passed through two tubes, L, L, containing sticks of caustic potash, and finally through two tubes, M, M, containing phosphoric oxide.

Fig. 3



The object of the two large alkaline towers was to retain oxides of manganese and carbon dioxide. The two tubes, J and K, containing potash of increasing concentration, served to diminish distillation of water from the towers to the stick potash tubes. After the apparatus had been in use for more than two years there was no sign of deliquescence either in the solid potash or in the phosphoric oxide.

When the washing and drying train had been set up it was exhausted by a water pump from three **T**-pieces simultaneously at N, O and P. Each of the permanganate tubes was then heated in turn, the train being exhausted between each oxygen filling. When all air had been removed the **T**-pieces were sealed off. After leaving the drying train the gas passed through the tap, Q, to the fractionating tube, R, where it was liquefied. When a sufficient quantity of liquid had been condensed the tap, Q, was closed, and a portion of the liquid was allowed to boil off and escape through the gauge, S. The second fractionating tube, T, which had been previously exhausted, was now cooled in liquid air, and the 3-way tap, V, was opened. On lowering the liquid air vessel from R a small quantity of liquid oxygen soon condensed in T. The 3-way tap was then turned so that the gas bubbled through its liquid. The object of this was to prevent superheating so that any higher-boiling impurities would be more effectively retained. A quantity of gas, washed by its own liquid, was allowed to escape by the gauge, W, or was removed by the pump. The next fraction, bubbled in the same way through its own liquid, was taken for the determination, and the residue in both fractionating tubes was rejected.

The Measuring Apparatus.

It may be taken as established by earlier workers that the ratio of the combining volumes is slightly greater than 2 when the gases are measured at normal temperature and pressure. Our procedure, in brief, has been to explode one volume of oxygen with rather more than two volumes of hydrogen, the variable and carefully measured excess over two volumes being sufficient in quantity to ensure a residue of hydrogen being left after synthesis. The gases were measured consecutively in the same apparatus. By working with hydrogen in excess, the possibility of the formation of such substances as ozone, hydrogen peroxide, or oxide of mercury, should be diminished or eliminated.

The final operation was to estimate the hydrogen residue, when the combining volumes could be calculated.

For measuring the gases at 0° C., and 760 mm. pressure, the method was the same as that used by GRAY and BURT(10) for the volumetric analysis of hydrogen chloride. In fact, some parts of the original apparatus were kindly lent to us by Dr. GRAY. The measuring pipette (fig. 4) consisted of a thick-walled glass bulb, A, of about 300 c.c. capacity, sealed to capillary tubes at either end of its vertical diameter. The lower capillary expanded into the dead-space, B, which was furnished with a glass point. The upper capillary, after a right-angle turn, led to the 3-way tap, C. The pressure of gas in the bulb was registered by the vertical distance between the mercury surface in the dead-space and the mercury surface in the upper chamber, D, of the manometer, which communicated with the dead-space as shown in the figure. The upper chamber of the manometer, of the same diameter as the dead-space,

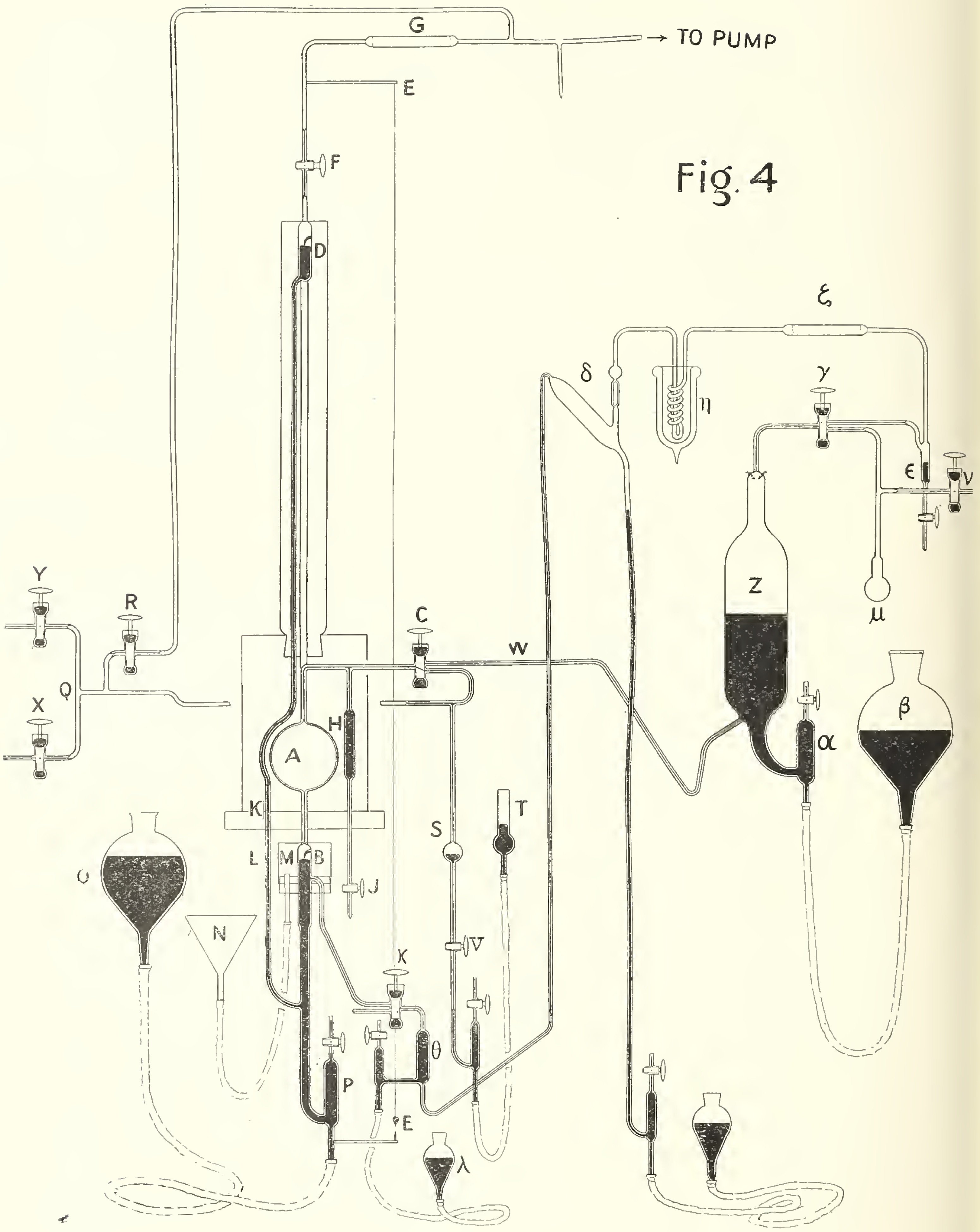


Fig. 4

(1·6 cm.), was also provided with a glass point. The vertical distance between the glass points was very nearly 760 mm., and this distance was maintained constant by means of a stout glass rod sealed at its upper end to the manometer chamber and at its lower to the elbow of the capillary connecting the bulb and the 3-way tap. The whole apparatus was rigidly fixed to a heavy iron bar with a tripod base, and the top of the bar was clamped to a staple driven into the ceiling. Any displacement from the vertical could be detected by the plumb-line, E, E, and corrected by means of levelling screws in the tripod base. The manometer head communicated with a mercury pump through the tap F, and the phosphoric oxide tube, G, so that the vacuum could be verified from time to time. Sealed to the capillary between the bulb and the 3-way tap was a capillary T-piece expanding into a tube of a few cubic centimetres capacity, H, which terminated at its lower end in another capillary, furnished with a tap, J. This tube, which was normally filled with mercury to the top, may be conveniently referred to as the volume-adjuster, since the capacity of the pipette could be increased to a small extent by withdrawing mercury from the tap, J.

The bulb, the volume-adjuster, and a portion of the manometer tube were enclosed in a tinned-iron bath with a stout brass base. The upper portion of the manometer was also enclosed in a bath constructed of a wide glass tube closed at the bottom by a rubber cork through which the glass rod and manometer tube passed. The lower bath somewhat overlapped the upper, so that by filling both baths with melting ice the whole system could be cooled to 0° C., with the exception of the dead-space and a piece of the capillary above it and the short column of mercury in the manometer from K to L.

On account of the difficulty of seeing the point it was inpracticable to surround the dead-space with ice. The small bath, M, was therefore filled with cooled brine by means of the funnel, N. It was found quite easy to secure a temperature within 0°·5 C. of zero when the final setting was made. Because of the small volume of the dead-space, (almost exactly 1 c.c.) a variation of this order did not affect the results. The mercury required for displacing gas from the bulb was contained in the reservoir, O. An air-catch, P, protected the pipette from any air leak at the rubber junction.

Calibration of the Pipette.

The volume of the bulb, dead-space, and connecting capillaries, from the tap, C, to the level of the glass point in the dead-space, was calibrated by means of mercury after the apparatus had been set up, but before the side tube leading to the manometer had been sealed on. For this purpose a stop-cock on capillary tubing was temporarily fused to the glass tubing below the dead-space.

The dead-space was calibrated separately. Mercury was introduced through the stop-cock until the meniscus was set to the point, the dead-space and tubing below it being immersed in a water-bath so that the temperature of the mercury could be recorded satisfactorily. This mercury was run out and weighed. A mark was next made on the capillary just above the dead-space; mercury was introduced again to the level of the mark, and this quantity was run out and weighed.

Weight of mercury from dead-space point to end of stop-cock.	Temperature.	Volume.
gr.	° C.	c.c.
(1) 192·14	21·5	14·188
(2) 192·17	20·5	14·188
(3) 192·20	20·0	14·189
	Mean . . .	14·188
Weight of mercury from mark on capillary to end of stop-cock.		
gr.		
(1) 205·76	21·5	15·194
(2) 205·84	19·0	15·193
(3) 205·90	18·0	15·195
	Mean . . .	15·194
Therefore volume of dead-space = 15·194 − 14·188 = 1·006 c.c.		

The pipette was now filled with mercury up to, but not including, the bore of the tap, C, and cooled to 0° C. with melting ice. Mercury was then run out from the tap to the mark on the capillary, care being taken that the initial and final temperatures of the warm mercury in the dead-space and tubing below it were the same.

Weight of mercury from 3-way tap to mark on capillary.	Temperature.	Volume.
gr.	° C.	c.c.
(1) 4160·03	0	305·986
(2) 4160·09	0	305·990
	Mean . . .	305·988
Total volume of pipette = 305·988 + 1·006 = 306·994 c.c.		

This value was checked by running out mercury in a single operation from the 3-way tap to the dead-space point.

Weight of mercury from 3-way tap to dead-space point.	Temperature.	Volume.
gr.	° C.	c.c.
4173·36	0 in bulb 21 in dead-space	306·996
	Mean total volume .	306·995

For our purpose it was unnecessary to determine the volume of the pipette with very great exactness. Let the volume be represented by x, and let $2x+y$ be the volume of hydrogen that unites with x of oxygen. Then the ratio of the combining volumes is $\frac{2x+y}{x}$, where x is more than three hundred times as great as y. A change of 0·5 c.c. in the value of x alters the ratio by only 1 part in 400,000.

No sensible error is introduced, therefore, by calling the volume of the pipette 307 c.c. in round numbers. Again, there was no need to reduce the mercury weighings to the vacuum standard, since the small volume increments (represented by y) were also estimated by running out mercury which was counterpoised by the same set of weights. These weights were carefully compared with each other, but the deviations from their face values were far too small to involve a significant correction.

Introduction and Measurement of the Gas.

The exit tubes from the hydrogen and oxygen trains united beyond the taps, X and Y, at the T-piece, Q. The common channel then divided again, one branch leading to the mercury pump through the tap, R, and the other to the measuring bulb. After the large bath had been filled with powdered ice, gas was allowed to enter the pipette, displacing mercury into the reservoir, O, until the mercury surfaces in the dead-space and manometer chamber were approximately set to the two points. The tap, X or Y, as the case might be, was then closed. The ice in the large bath was pressed down and replenished, and the upper bath was also charged with ice. Finally, both baths were filled with ice-cold water, and the dead-space was cooled with brine. The fine adjustment was now made by means of the pressure-adjuster, S. By holding the small reservoir, T, at a suitable height and rapidly turning the tap, V, minute quantities of gas could be introduced into or withdrawn from the pipette. By the alternate manipulation of the pressure-adjuster and of the screws controlling a wooden clip which compressed the rubber tubing connecting the reservoir to the pipette, the mercury meniscuses were set to their respective points. The tap, C, was then closed.

In this manner a definite volume of gas at a temperature of 0° C. and a pressure of 760 mm. could be obtained repeatedly.

Transference and Synthesis.

By raising the reservoir, O, and opening the tap, C, the gas in the pipette was made to pass through the capillary tube, W, into the explosion vessel, Z, which was filled with mercury. The end of the capillary inlet tube was fused as an inserted join through the base of the explosion vessel, and as the gas bubbled in, the mercury was displaced through the air-trap, α, to the reservoir, β. The explosion vessel, about a litre in capacity, consisted of a wide glass cylinder, 22 cm. long and 8 cm. in diameter, drawn out at its upper end to a narrow neck, 6 cm. long and 18 mm. in diameter. Near the apex of the neck two platinum electrodes were sealed through the glass, the portions of wire inside the tube being glass-covered nearly to their tips. A capillary tube leading to the 3-way tap, γ, afforded exit from the explosion vessel. This tube remained full of mercury down to the top of the spark-gap during the entry and explosion of the gases.

The explosion vessel was supported by a wooden pedestal screwed on to the bench. The top of the pedestal was roughly shaped to fit the base of the cylinder, the pressure being evenly distributed by a packing of cotton wool.

When one measured volume of hydrogen had been transferred to the explosion vessel, the pipette was filled again and the operation repeated. In order to secure a small excess of hydrogen, a few cubic centimetres of mercury were withdrawn from the volume-adjuster during one of the fillings, so as to increase the volume of the pipette. By weighing this mercury the excess volume could be accurately estimated. When about half the gas had been expelled from the pipette, the tap, C, was closed and the reservoir, O, was lowered so as to reduce the pressure in the system. A crucible containing mercury was then brought up to submerge the capillary end of the volume-adjuster, and the tap, J, was opened until mercury rose to the level of the T-piece. The rest of the gas was then transferred.

The connecting tubes between the pipette tap and the gas trains were now exhausted and washed out with oxygen, after mercury had been taken through the lower bore of the tap, C, to expel the small quantity of hydrogen imprisoned there. The pipette was then filled with oxygen and the measured volume of gas was transferred to the synthesis vessel in successive portions, the addition of gas being continued until the passage of a spark caused an explosion. In practice we found that 600 c.c. of hydrogen and 300 c.c. of oxygen could be united conveniently by admitting the oxygen in seven fractions. The pressure in the explosion vessel was kept nearly atmospheric until six-sevenths of the oxygen had been fired, but, before the final explosion, the reservoir, β, was lowered, since the mixture now approximated to electrolytic gas, and there would have been some risk of shattering the vessel.

The small residue of wet hydrogen was compressed into the neck of the explosion vessel and sparked for a few moments. In order to collect any gas bubbles caught between the mercury and the glass, the reservoir, β, was lowered until most of the mercury had left the cylinder. A paper cone, mounted on a split cork, was fitted round the neck of the explosion vessel, and charged with a mixture of acetone and solid carbon dioxide. The water rapidly condensed as a film of ice on the walls of the neck, and, at the very low pressure in the vessel, the quantity of gas retained by the ice must have been negligibly small. When every trace of water had disappeared, mercury was allowed to rise to the bottom of the neck, and the dry hydrogen was sparked again for several minutes to eliminate any oxygen that might have escaped combination at the final explosion. Since any water vapour formed would at once be removed as ice, there was little chance of the reaction $2H_2+O_2 = 2H_2O$ being reversed.

Measurement of the Hydrogen Residue.

The tubing of the reservoir, β, was now clipped, and the tap, γ, turned to admit the dry hydrogen into the little pump, δ. The mercury thread in the capillary was shot into the trap, ϵ, and the gas passed to the pump through the tube, ζ, containing phosphoric oxide which had been distilled in oxygen, and the spiral, η, which was cooled in liquid air. Any impurities condensed in this spiral could be pumped out and examined after all the hydrogen had been removed. The delivery tube of the pump, made of very fine-bore capillary was turned up and sealed as an inserted join into the small collecting vessel, θ.

This vessel carried a 3-way tap, κ, communicating on the one hand with the air, and on the other with the pipette by means of a capillary T-piece below the dead-space. The little pump was worked "tight," and any gas bubbles adhering to the turned-up end of the delivery tube were liberated by lowering the reservoir, λ. The pipette was now filled with hydrogen from the train, and a setting was made in the manner already described. As soon as the points were set the tap, C, was closed, and the hydrogen in θ was driven over into the pipette by raising the reservoir, λ, and opening the tap, κ. The mercury in the dead-space was depressed, and the original pressure was recovered by withdrawing mercury from the volume-adjuster until both points were set again. From the weight of mercury taken out, the volume of the hydrogen residue could be calculated.

At first sight, this method of measuring a few cubic centimetres of gas may appear needlessly cumbrous, but in actual practice we found it both convenient and accurate. It had this great advantage, that no new pressure standard, with its possibly attendant errors, was introduced; the hydrogen residue was measured under precisely the same conditions as the gases before synthesis.

Removal of the Water.

After the hydrogen residue had been pumped out of the explosion vessel the tap, γ, was closed and the film of ice in the neck allowed to melt. On cooling the bulb, μ, in liquid air and turning the tap, γ, the water distilled slowly from the neck to the bulb. When the removal of water was judged complete, the tap, γ, was closed and the clip on the tubing of the reservoir, β, opened to allow mercury to fill the vacuous neck of the explosion vessel. The click with which the mercury thread in the capillary met the tap-barrel bore witness to the absence of gas or water-vapour. After each experiment the bulk of the water collected in μ was removed by exhausting with a water pump at the T-piece, ν, while the bulb was warmed with a flame.

First Series of Determinations.

Both gases were made by electrolysis: the hydrogen was purified by exposure to charcoal cooled in liquid air; the oxygen was liquefied and fractionated as described on p. 399. To ensure the removal of moisture from the glass surfaces, the trains were left exhausted for a month and then washed out with hydrogen and oxygen respectively. The measuring pipette, explosion vessel, and small pump were also washed out with hydrogen, and the pentoxide tube, ζ, was warmed during passage of the gas.

To gain experience in manipulative technique, five preliminary determinations were carried out. Of the fourteen succeeding experiments, two (Nos. 8 and 9), were rejected. In these two experiments the normal procedure for purifying hydrogen was modified; instead of passing a stream of the gas through the cooled charcoal U-tube into the pipette, we allowed the saturated charcoal to warm up, and took the first fractions of the gas expelled. The results obtained were much higher than any others in the series.

The volume of oxygen taken for synthesis was 307 c.c. in all cases; the volume of hydrogen was 614 c.c. + a small, variable excess. Column 1 of the following table gives this excess as determined by the weight of mercury withdrawn from the volume-adjuster in one of the two hydrogen fillings. Column 2 gives the volume of the hydrogen residue after explosion, as determined by the weight of mercury withdrawn from the volume-adjuster in the final setting. Column 3 gives the difference between the volumes in the first two columns, representing the excess over 614 c.c. of hydrogen required to combine with 307 c.c. of oxygen. Column 4 gives the ratio of the combining volumes, and column 5, the atomic weight of hydrogen (0 = 16), computed from MORLEY's value for the density ratio $\left(\frac{1\cdot42900}{0\cdot089873}\right)$.

If R is the ratio of the combining volumes, and A the reciprocal of the density ratio, the atomic weight of hydrogen = 8RA, so that any error in either ratio implies the same percentage error in the atomic weight.

TABLE I.

	1. Hydrogen excess.	2. Hydrogen residue.	3. Difference.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.
	c.c.	c.c.	c.c.		
1	4·316	3·439	0·877	2·00286	1·00771
2	4·072	3·140	0·932	2·00304	1·00780
3	4·755	3·877	0·878	2·00286	1·00771
4	4·271	3·366	0·905	2·00295	1·00776
5	1·670	0·750	0·920	2·00300	1·00778
6	5·717	4·844	0·873	2·00284	1·00771
7	2·962	2·044	0·918	2·00299	1·00778
10	2·202	1·309	0·893	2·00291	1·00774
11	2·565	1·576	0·989	2·00322	1·00790
12	2·605	1·699	0·906	2·00295	1·00776
13	2·015	1·179	0·836	2·00272	1·00765
14	3·231	2·340	0·891	2·00290	1·00774
			Mean	2·00294 ±0·00002	1·00775
			Maximum deviation, 1 in 4000		

In the first few rejected experiments a small quantity of gas was condensed from the hydrogen residue in the spiral, η. This gas was measured in the calibrated capillary at the top of the collector, θ. In the first experiment it amounted to about 10 c.mm., falling to 2 c.mm. to 3 c.mm. in the second. Throughout the rest of the series the quantity was less than 1 c.mm. This gas was most probably carbon dioxide, produced by combustion on the walls of the explosion vessel of traces of organic impurities which previous cleaning treatment had failed to remove. Since the capillary exit tube from the explosion vessel was always full of mercury while the gases were being combined, there was no possibility of the flame reaching the grease on the tap, γ.

Second Series.

Hydrogen, generated as in series 1, was purified by passage through the walls of a palladium tube.

Oxygen was made and purified as in series 1.

After four or five determinations, yielding somewhat discordant results, a crack was discovered in the palladium tube. A new tube, made from fused metal, was then set up. Of the following twelve experiments, two (Nos. 5 and 11), were rejected; No. 5, because, owing to an accident, the determination was interrupted in the middle, and only completed after an interval of several days; No. 11, because the accuracy of one of the settings was suspected at the time on account of the light being bad.

The five columns of figures in Table II. correspond to those in Table I.

TABLE II.

	1. Hydrogen excess.	2. Hydrogen residue.	3. Difference.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.
	c.c.	c.c.	c.c.		
1	2·026	1·147	0·879	2·00286	1·00772
2	3·331	2·440	0·891	2·00290	1·00774
3	3·687	2·794	0·893	2·00291	1·00774
4	2·233	1·359	0·874	2·00285	1·00771
6	5·641	4·777	0·864	2·00281	1·00769
7	3·871	2·960	0·911	2·00297	1·00777
8	4·738	3·822	0·916	2·00298	1·00778
9	3·926	3·000	0·926	2·00302	1·00779
10	2·835	1·934	0·901	2·00293	1·00775
12	2·958	2·062	0·896	2·00292	1·00774
			Mean	2·00292 ±0·000014	1·00774
			Maximum deviation, 1 in 10,000		

Before the next series of determinations the palladium tube, which was showing some signs of weakness, was cut down and sent away to be repaired.

Third Series.

Hydrogen was made and purified as in series 2, except that on leaving the electrolysis vessel it passed through a tube containing palladium black. Oxygen was obtained from potassium permanganate as described on pp. 399–401.

At this stage of the research we had a great deal of trouble owing to the appearance of condensible gas in the hydrogen left after explosion, accompanied by discrepant and much lower results. The quantity of gas condensed in the spiral, η, varied from 40 c.mm. to nearly 300 c.mm. in different experiments. It was completely soluble in a drop of potash or baryta solution, giving a white precipitate in the latter case. The source of the impurity was at first believed to be the oxygen generated from permanganate, since all other conditions were apparently the same as in series 2, but liquefaction and fractionation of much larger quantities of oxygen produced no improvement.

Any impurities accompanying the oxygen must have been sufficiently volatile to escape condensation in the fractionating tubes. To test whether oxygen could retain or acquire carbon dioxide, as such, after leaving the fractionating train, a considerable volume was pumped through the cooled spiral, η. Nothing was retained by the spiral. KAMMERLING ONNES ([11]) has shown that, at the boiling point of oxygen, the vapour pressure of carbon dioxide is about 6×10^{-6} mm. of mercury, so that little could escape condensation when exposed to a large surface of glass cooled in liquid air. It seemed just possible that oxidation of dust in the permanganate tubes might give rise to carbon monoxide, a gas about as difficult to separate from liquid oxygen by fractional distillation as nitrogen would be. Some experiments carried out by Mr. J. N. GREENWOOD indicate that if any carbon monoxide is present in permanganate oxygen, the quantity is less than 1 part in 40,000 by volume, even when no precautions are taken to avoid the presence of dust in the decomposition tube.

We next considered the possibility of impurities in the explosion vessel. There was no question of grease finding its way back from the tap, γ, because mercury and gas travelled always in the opposite direction. The pipette tap was separated from the explosion vessel by more than half a metre of capillary tubing in which there were several bends. Any grease carried by a mercury thread through a tap-bore is usually deposited in the first few centimetres of connecting tube. In order to obviate any possible risk of contamination in this way, the device illustrated in fig. 5 was adopted. Two vertical capillary tubes, A and B, were sealed to the transference capillary at C, as close together as possible : A was provided with a tap, and B was connected with a mercury reservoir, D, through an air-trap, E. The tube, B, had no tap, but the flow of mercury through it was controlled by a screw-clip on the reservoir tubing.

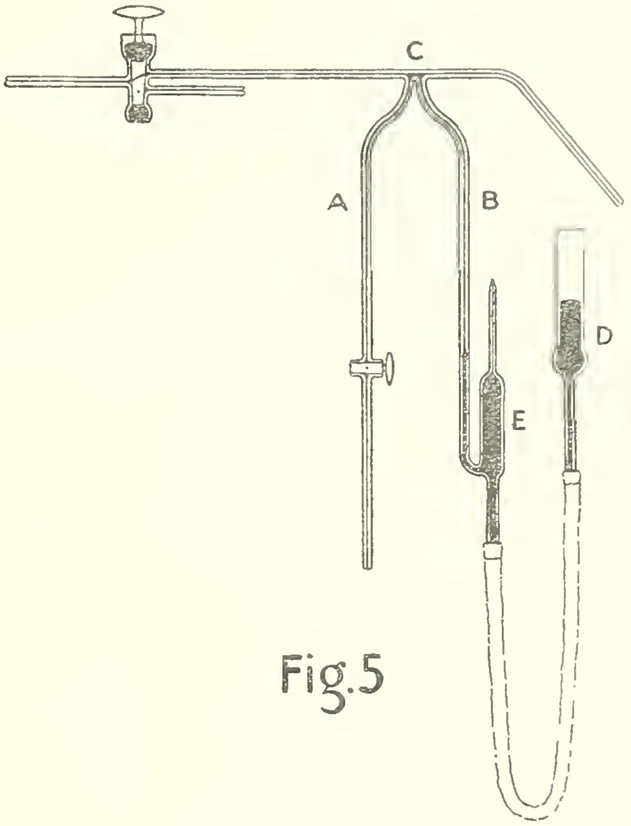


Fig. 5

All mercury that passed through the pipette tap was withdrawn by the tube, A. At the end of the process of transferring gas from the pipette to the explosion vessel, the mercury thread following the gas through the pipette tap and along the capillary was checked at C. The gas remaining in the capillary between C and the explosion vessel was then driven over by clean mercury from the reservoir, D.

To remove any grease that might have previously found its way there, the explosion vessel itself was cut down and drastically cleaned by consecutive treatment with stannous chloride and strong hydrochloric acid, and a hot solution of chromic anhydride in fuming nitric acid. After the acid had been washed out, the final content of distilled water was replaced by dust-free air drawn in over cotton-wool. The vessel was then dried at room temperature in a stream of air passed over calcium chloride and filtered through cotton-wool.

On continuing the determinations, condensible gas was still found in the hydrogen residue. The only sources of impurity yet to be examined was the hydrogen. A glass spiral was inserted in the train between the palladium tube and the pipette, and cooled in liquid air during the filling. A small quantity of gas was condensed in the spiral, and the amount of impurity in the hydrogen residue was diminished, though not entirely eliminated, by this treatment; facts which at once suggested a flaw in the palladium tube. The tube was accordingly cut down and examined, and a crack was discovered. The phosphoric oxide in the drying trains had not been distilled in oxygen, and was probably the source of contamination. It is of interest to note that hydrogen passed over impure phosphoric oxide apparently contains some carbon compound which is not condensed at the temperature of liquid air; perhaps carbon monoxide. A new palladium tube, the third described in the preface, was procured and set up, and in the following series of determinations, the amount of condensible gas in the hydrogen residue was absolutely negligible. In some

Table III.

	1. Hydrogen excess.	2. Hydrogen residue.	3. Difference.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.
	c.c.	c.c.	c.c.		
1	3·213	2·323	0·890	2·00290	1·00773
2	3·116	2·221	0·895	2·00292	1·00774
3	3·990	3·092	0·898	2·00292	1·00775
4	3·128	2·240	0·888	2·00289	1·00773
5	2·630	1·754	0·876	2·00285	1·00771
6	3·424	2·521	0·903	2·00294	1·00776
7	2·495	1·584	0·911	2·00297	1·00777
8	3·247	2·341	0·906	2·00295	1·00776
9	3·573	2·655	0·918	2·00299	1·00778
10	2·552	1·675	0·877	2·00286	1·00771
			Mean . . .	2·00292 ±0·00001	1·00774
			Maximum deviation, 1 in 14,000		

experiments in this series, a very large quantity of oxygen was liquefied and fractionated; in others, only just enough for the purpose. The concordance was better than in series 1 and 2, the maximum deviation among ten consecutive determinations being less than 1 part in 14,000.

The means of series 1, 2 and 3 differ by only 1 part in 100,000. The final mean, taking into account the probable error of each series, is 2·00292, with a probable error of less than ±4 parts in 1,000,000. The corresponding atomic weight for hydrogen is 1·00775. Since the oxygen was obtained from two totally distinct sources, and the hydrogen, though always derived from the electrolysis of barium hydroxide, was purified by two essentially different methods, the close agreement of the means of the three series suggests that the purity of the gases reached a high standard. Before accepting these values, however, it was necessary to consider the possibility of systematic errors inherent in the methods employed. One such constant error had already been detected. When a measured volume of gas was displaced from the pipette by mercury, a small bubble was always trapped in the dead-space, at the region of insertion of the glass point. Since, after the expulsion of the second hydrogen filling, oxygen was admitted without first washing out the pipette, the oxygen was contaminated with this small quantity of hydrogen. This implied a corresponding deficit of oxygen, the nett result being an excess of hydrogen in the residue after explosion equal to three times the volume of the original bubble.*

By closing the pipette tap after removal of the gas, and lowering the reservoir, O, this bubble escaped into the vacuum so formed, and could be measured in the pipette capillary which was calibrated for the purpose. From a number of measurements with both hydrogen and oxygen the volume of the imprisoned bubble proved to be remarkably constant. As a mean of six experiments, agreeing to within 1 c.mm., this volume was found to be 6·5 c.mm., when corrected to normal temperature and pressure. This implied an excess of 19·5 c.mm., in the hydrogen residue, which would make the ratio of the combining volumes (and the atomic weight of hydrogen) too low by 33 parts in 1,000,000. The alteration involved was much smaller than the variations among the individual determinations, but the correction was justifiable since it was constant both in magnitude and sign. The corrected values for the final means become 2·00299 and 1·00778.

Fourth Series.

To test the validity of this correction we proceeded to carry out a further series of determinations in which the imprisoned hydrogen bubble was removed before the introduction of the oxygen.

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* The final hydrogen filling, which was contaminated in a similar way with a trace of oxygen, was removed by the mercury pump at the end of each determination.

Hydrogen was prepared and purified as in series 3: oxygen was obtained both by electrolysis and by heating permanganate, so that large quantities of gas were rapidly available for fractionation. Electrolytic oxygen, accumulated from time to time in a $2\frac{1}{2}$-litre storage bulb, entered the main train at the T-piece (Z, fig. 3), after being dried over calcium chloride, and phosphoric oxide.

In this series, and in the preceding one, an attempt was made to measure the temperature of the mercury in the short exposed portion of the manometer column that projected below the bath (K to L, fig. 4). For this purpose, a small thermometer, graduated in tenths of a degree, was fastened by fine copper wire to the manometer tube, and the whole was wrapped in cotton-wool. The temperature registered by this thermometer was probably proportional to, if not identical with, the temperature of the mercury in this region of the manometer. The readings varied with the room temperature and length of time during which the system had been in ice. The main controlling factor was the temperature of the room. Since the distance between the two glass points to which the mercury meniscuses were set was constant, any rise in temperature of the mercury in the manometer implied a diminution of pressure and corresponding increase in volume of the gas in the pipette. An empirical value for the temperature effect was obtained by filling the pipette with gas, making a setting and noting the temperature of the thermometer, and then repeating the measurement when the temperature was a degree or so higher. From the weight of the few drops of mercury that had to be withdrawn from the volume-adjuster to set the points on the second occasion, it was possible to estimate the increase in the volume occupied by the gas per unit rise of temperature as registered by the thermometer.

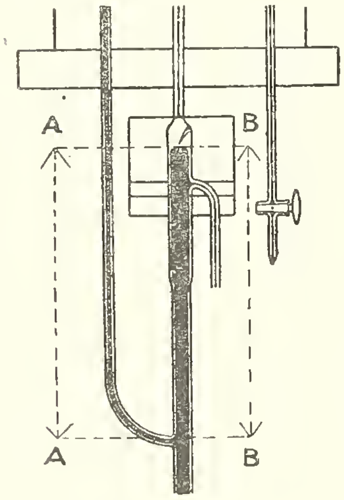


Fig 6

The mean of several very concordant results was 21 c.mm. per degree. Now the length of the exposed portion of the manometer was about 4 cm., and a change of 1° C. in the temperature of this length of mercury could not produce so large an effect. In fig. 6 the two columns of mercury, AA and BB, only equalise each other when their temperature is the same. All this region was packed in cotton-wool, the tubing below the dead-space being the more thickly coated. The mercury in A would be more sensitive to temperature changes than the larger bulk of better insulated mercury in B, so that part of the measured effect may have been due to relative temperature change in this part of the system.

In any case, the effect on the results is very small, since the room temperature seldom varied half a degree during a determination. The application of the correction to the results of series 3 improves the concordance a little without altering the mean.

In series 4 the temperature variations were greater. In order to protect the apparatus from the warmth of the observer's body, a sheet of asbestos was fastened in front of the manometer and tubing below the dead-space, with the result that the cooling effect of the ice-baths above came more into play, and the temperature registered by the thermometer was lower the longer the system had been in ice. Consequently the hydrogen fillings, which were made first in the day, contained relatively too little gas. The result of applying the correction to series 4 was to lower the mean by 1 part in 50,000.

The following table gives the results of series 4 : two additional columns, 6 and 7, give the values for the ratio and the atomic weight when the small correction is applied.

TABLE IV.

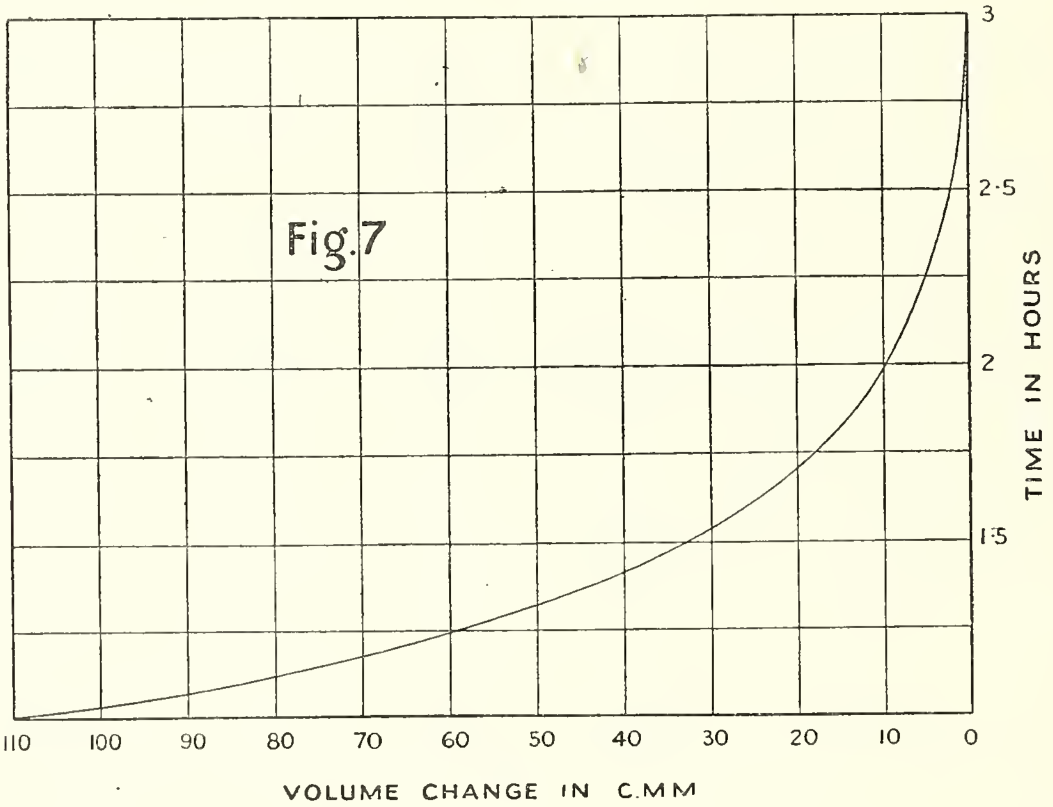
	1. Hydrogen excess. c.c.	2. Hydrogen residue. c.c.	3. Difference. c.c.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.	6. Ratio of combining volumes.	7. Atomic weight of hydrogen.
1	2·443	1·527	0·916	2·00298	1·00778	2·00300	1·00779
2	3·717	2·827	0·890	2·00290	1·00773	2·00284	1·00771
3	2·846	1·903	0·943	2·00307	1·00782	2·00299	1·00778
4	3·589	2·614	0·975	2·00318	1·00787	2·00305	1·00781
5	3·453	2·507	0·946	2·00308	1·00783	2·00309	1·00783
6	3·311	2·410	0·901	2·00293	1·00775	2·00288	1·00773
7	3·895	2·945	0·950	2·00309	1·00783	2·00306	1·00781
8	2·945	2·015	0·930	2·00303	1·00780	2·00301	1·00779
9	2·015	1·052	0·963	2·00314	1·00785	2·00307	1·00782
10	3·448	2·521	0·927	2·00302	1·00780	2·00310	1·00784
			Mean. . . .	2·00304 ± 0·00002	1·00781	2·00301 ± 0·00002	1·00779
			Mean deviation, 1 in 7000.				

The mean value of the ratio in column 6 differs by only 1 part in 100,000 from the final mean of the first three series when this is corrected for the imprisoned bubble.

It may be noted in the above table that without experiments 2 and 6 the maximum deviation in column 4 is 1 part in 10,000, and in the corrected values in column 6, only 1 part in 18,000.

The explanation of the two low results is to be found in another temperature error which affects all four series. The final setting of a determination had sometimes been repeated on the following day, with the object of testing the accuracy of the measurement. On such occasions it was noticed that the volume of gas in the pipette had apparently increased, unless the bath had been iced for some time before the reading was made. It was therefore necessary to make a careful investigation of the time needed for temperature equilibrium to be established after ice had been put in the pipette bath. The problem was attacked in two ways: in the first place, we made a series of measurements of the gas in the pipette on consecutive days, the interval of time between the introduction of ice and the setting being decreased from day to day. The volume expansion corresponding to these time intervals was obtained from the weight of mercury that had to be taken from the volume-adjuster in order to set the points.

In the second place, the pressure change of the gas in the pipette was measured at constant volume by making a setting a short time after the introduction of ice, and then, keeping the lower mercury meniscus set to the point in the dead-space, measuring the increase in distance between the upper meniscus and its point with lapse of time. This was done with a reading telescope, fitted with a Hilger micrometer eye-piece. The two methods yielded concordant results which were checked at a later date by a large number of similar measurements made with a cathetometer. In fig. 7, volume change in cubic millimetres is plotted against the time, in hours, during which the bulb had been in ice, and the resulting curve indicates that nearly three hours were required to establish temperature equilibrium.*



Now each complete determination occupied from twelve to fifteen hours and was carried through in two consecutive days. The normal procedure was to measure and

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* The unexpectedly long time taken by the gas to attain temperature equilibrium may have been due to the fact that the base of the bulb was supported by a small rubber cork which protected the glass over a small area from direct contact with the ice.

combine the gases on the first day and leave the wet hydrogen residue safely imprisoned between mercury surfaces in the explosion vessel over night. The residual hydrogen was measured on the following day. The order of operations at the beginning of each day was identical. First of all the pipette was cooled with ice; then hydrogen was admitted, the upper bath iced and a setting made. During the rest of the day the ice in the pipette bath was never removed, but was pressed down and replenished immediately before each reading. On the second day, as soon as the first hydrogen setting was accomplished, the residue in the explosion vessel was dried, sparked and transferred to the pipette; the ice in the baths was then replenished and the final setting was made. The last two measurements, therefore, were separated by a considerable interval of time. Of the five gas measurements required in each determination, only two, namely the first of each day, fell within the three-hour period preceding the establishment of equilibrium. Consequently, in both these measurements the quantity of hydrogen actually taken was less than the quantity assumed in the calculation. The error in each case makes the result too high.

The accurate evaluation of the correction involves a knowledge of the time interval between the introduction of ice and the completion of the setting. Although the time had always been noted when a setting was made, the same precaution had, unfortunately, seldom been taken at the moment of iceing the bulb. There was little variation, however, in the time occupied by the intermediate operations, which in series 3 and 4 had become almost mechanical. In series 3, the most uniform as regards method of procedure, and the most concordant in results, the time interval as actually measured in several determinations was one and three-quarter hours, and the mean time for the whole series was certainly within a few minutes of this. It may be seen from the curve (fig. 7) that when the bulb had been in ice for an hour and three-quarters, the volume of the gas was still 18 c.mm. in excess of its final value, so that had the measurement been delayed till contraction was complete, an additional 18 c.mm. of gas must have been introduced to achieve the setting. Since the calculation is based on this assumption, the nominal volume of hydrogen taken for synthesis must be diminished by 18 c.mm., and, by parity of reasoning, the nominal volume of the residue must be increased by the same amount. The net result is a diminution of 36 c.mm. in the volume of hydrogen required to combine with 307 c.c. of oxygen. This implies a reduction of 6 parts in 100,000 in the values for the ratio and the atomic weight.

In series 4, an attempt to estimate the above time intervals for each individual experiment led to the same average reduction. In experiment 6, for example, the oxygen measurement, instead of being made at the end of the first day when the bulb had been in ice for many hours, was made on the following morning. The temperatures of the oxygen and hydrogen were therefore more comparable, and the resulting correction was small. In several of the other determinations the correction was larger than in series 3. As regards series 1 and 2 a similar correction was necessary. The time interval in question was in most cases rather greater, since the hydrogen took longer to obtain. On the other hand, the correction for the imprisoned bubble was probably a little smaller. The presence of this bubble had escaped observation in the early part of the research, owing, perhaps, to the fact that the mercury in the pipette was very clean and therefore trapped a smaller quantity of gas.* With long continued use and contact with rubber tubing, inevitable slight fouling occurred.†

That the average volume of the imprisoned bubble was increasing very slightly during the later stages of the research, was proved by actual measurement. Both these opposing errors may therefore have been smaller in the earlier series. Taking into account the very close agreement of the means it seemed fairest to apply the same "contraction" correction throughout, and to reduce the means of all four series by 6 parts in 100,000. Collecting all the results we have :—

	Series 1.	Series 2.	Series 3.	Series 4.
	2·00294 ± 0·00002	2·00292 ± 0·000014	2·00292 ± 0·00001	2·00301 ± 0·00002
Corrected for imprisoned bubble .	2·00301	2·00299	2·00299	2·00301
Corrected for "contraction" . . .	2·00289	2·00287	2·00287	2·00289

The arithmetic mean of the ratios in the last line is 2·00288, and the corresponding atomic weight of hydrogen is 1·00772.

Fifth Series.

Since the magnitude of the "contraction" correction was a little uncertain, a fifth series of determinations was undertaken. In this series no measurement was made until the pipette had been in ice for at least three hours. The gases were made and purified exactly as in series 4, and the trapped hydrogen bubble was removed before the oxygen filling. To eliminate variations in the temperature of the mercury in the exposed portion of the manometer, a small subsidiary bath, constructed of the two halves of a short brass cylinder, mounted on a split cork, was fitted to the manometer tube in this region. This bath was filled with powdered ice immediately before each reading was made. By a modification of procedure on the second day the two final settings were made one immediately after the other so that there was no need to re-ice the baths. As soon as the first setting was finished, the hydrogen residue, previously accumulated in the collector, was at once admitted, and the necessary adjustment made by running out mercury. Of the thirteen experiments in this series, one, No. 6, was

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[*] Before its introduction into the apparatus the mercury was purified from foreign metals by distillation and by washing with mercurous nitrate solution, and was finally dried by heating to 120° C.

[†] The tubing used was of a special kind designed to resist attack by mercury.

rejected. In this experiment, when the tap on the explosion vessel was opened to admit the hydrogen residue to the pump, the mercury thread in the capillary beyond the tap broke up into a series of globules which settled down and obstructed the passage of the gas. To remove them it was necessary to heat the capillary strongly with a flame, and since the glass in this region was contaminated with tap-grease, some chemical action may have occurred.

Table V.

	1. Hydrogen excess.	2. Hydrogen residue.	3. Difference.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.
	c.c.	c.c.	c.c.		
1	3·428	2·575	0·853	2·00278	1·00767
2	3·461	2·585	0·876	2·00285	1·00771
3	3·080	2·219	0·861	2·00280	1·00769
4	3·131	2·242	0·889	2·00290	1·00773
5	3·078	2·176	0·902	2·00294	1·00775
7	3·222	2·351	0·871	2·00284	1·00770
8	3·855	2·986	0·869	2·00283	1·00770
9	4·339	3·429	0·910	2·00296	1·00777
10	3·160	2·274	0·886	2·00289	1·00773
11	3·000	2·090	0·910	2·00296	1·00777
12	3·155	2·268	0·887	2·00289	1·00773
13	3·141	2·276	0·865	2·00282	1·00769
			Mean	2·00287 ±0·00001	1·00772

Maximum deviation, 1 part in 11,000.

The mean is practically identical with the corrected mean of the first four series, so that the estimate of the "contraction" correction is satisfactorily confirmed.

Although, in this series, no uniformity of procedure was adopted as regards the distribution of the gas measurements over the two days, examination of the results reveals no discrepancies attributable to this cause.

In experiments 1, 3, 9, 11 and 13, for example, the oxygen was measured on the afternoon of the first day, whereas in experiments 2, 4, 5, 8, 10 and 12, it was measured on the morning of the second day; yet the mean result for each group is the same. Experiment 7 was completed in a single day.

Except for the longer interval between iceing and setting, the presence of the small subsidiary ice bath on the manometer tube and the juxtaposition of the two final measurements constituted the only difference from series 4. The lower results of series 5 cannot be attributed to the presence of the little ice bath since the volume contraction curve was found to be the same whether this portion of the manometer was at room temperature or at 0° C. As the bath was used in every gas measurement, the effect of the resulting small increase in the quantity of gas required to fill the pipette cancels out.

The possibility of a small error, due to the difference of procedure in the two final measurements, was suspected on theoretical grounds. Before admitting the hydrogen residue to the pipette, the mercury in the dead-space was always lowered to the level of the capillary T-piece at which the gas entered. The mercury immediately below the dead-space and at the same level in the manometer was cold owing to the brine and the ice baths respectively. The result of lowering the pipette reservoir, therefore, was to bring cold mercury into the tubing below the dead-space and into the lower part of the manometer. The glass in these regions was cooled and if, on raising the mercury again, temperature equilibrium was established more rapidly in the manometer tube (see p. 414), the points would no longer be set. Moreover, if these assumptions are correct, the effect should be greater the higher the temperature of the room. Now the room temperatures at the determinations in series 5, ranged from 11°·5 C. to 13°·5 C., and averaged about 12° C. Examination of the experiments showed no connection between the temperature of the room and the value of the result.

A series of blank experiments was then undertaken when the temperature of the room was between 17° C. and 18° C. A setting having been made, the mercury was lowered for a period comparable to that required for admitting the hydrogen residue in an actual determination. On raising the pipette reservoir again it was found that mercury had to be taken from the volume-adjuster in order to set the points. The mean volume of mercury withdrawn in four very concordant experiments was 30 c.mm., so that actual determinations carried out at this room temperature would have been 1 part in 20,000 too low. The experiment was repeated at a room temperature of 16° C., when the volume of mercury withdrawn was only 10 c.mm. The inference is that, at the room temperatures obtaining in series 5, the correction would have been negligibly small, and this is confirmed by the above-mentioned fact that differences of 2° C. in this temperature region had no detectable influence on the results. It was unfortunately impossible to make blank experiments at these lower temperatures, unless we had waited for the winter.

The error just discussed does not affect the first four series, where, after the hydrogen residue had been admitted, and a rough adjustment made by running out mercury, the ice in the baths was replenished before the final setting. During this time interval the normal temperature conditions of the mercury in the tubes below the dead-space level would have been established again.

For the reasons mentioned in the preface an excess of hydrogen had been taken in all our experiments. It does not seem probable that any constant error would be involved by this practice, but the point was tested by carrying out a few determinations with oxygen in excess.

The preparation and purification of the gases and all subsequent precautions were the same as in series 5.

First of all, exactly two volumes of hydrogen and one volume of oxygen were exploded and the small residue of oxygen measured. In three other experiments a slightly greater proportion of oxygen was taken. The volume of hydrogen was 614 c.c. in all cases. The oxygen residue was estimated in exactly the same way as the hydrogen residue. It would have been more logical to fill the pipette with oxygen instead of hydrogen, which was selected because it was more easily procurable. On mixing 1 or 2 c.c. of oxygen with 300 c.c. of hydrogen, the resulting volume is not strictly additive, but the deviation, though not exactly determinable from existing data, is probably very small.

In these four experiments a new phenomenon was observed. In each case, after the final explosion in which oxygen had been present in excess, brown stains were noticed on the walls of the explosion vessel. These stains were presumably oxide of mercury since they gradually disappeared when mixtures containing an excess of hydrogen were detonated in the vessel. If a significant quantity of oxygen was fixed in this way, the value of the ratio would be too low. It was a moot point whether it was advisable to spark the dried oxygen residue. Coward (12) has shown that, when the pressure is low, traces of uncombined hydrogen and oxygen remain after detonating electrolytic gas. On the other hand, sparking might lead to the formation of ozone. In one case the result would be too high; in the other too low. The treatment in this respect was varied in the different experiments as follows:—

Example 1.	Example 2.	Example 3.	Example 4.
0·5 mins., sparking.	No sparking.	0·75 mins., sparking.	3 mins., sparking.

It is significant that the result of experiment 2 was the highest. It should be mentioned here that nothing was condensed when the oxygen residue was pumped through the liquid-air-cooled spiral. In the following table columns 1 and 2 represent the surplus volume of oxygen taken and the residue of oxygen left after explosion, respectively. Column 3 gives the difference between the first two columns, representing the volume by which 307 c.c. of oxygen must be diminished to be chemically equivalent to 614 c.c. of hydrogen.

Without laying any particular stress on these results it may be claimed that they do not suggest the presence of a constant error in the earlier experiments. We therefore conclude that the ratio of the combining volumes of hydrogen and oxygen is represented with a high degree of probability by the figure

2·00288 at 0° C., and 760 mm. pressure,

which differs from the value of Scott by only 3 parts in 200,000.

TABLE VI.

	1. Oxygen excess.	2 Oxygen residue.	3. Difference.	4. Ratio of combining volumes.	5. Atomic weight of hydrogen.
	c.c.	c.c.	c.c.		
1	0	0·428	0·428	2·00279	1·00768
2	1·533	2·021	0·488	2·00318	1·00788
3	1·084	1·551	0·467	2·00305	1·00781
4	0·508	0·933	0·425	2·00277	1·00767
			Mean	2·00295	1·00776
		Maximum deviation, 1 in 5000.			
		Omitting experiment 2, mean . .		2·00287	1·00772
		Maximum deviation, 1 in 7000.			

The ratio may be calculated from compressibility measurements. If the compressibility coefficient of hydrogen at 0° C., between 0 and 1 atmospheres, is taken as $+0{\cdot}00054$ (the mean of the values obtained by RAYLEIGH, JAQUEROD and SCHEUER, and CHAPPUIS) and the corresponding coefficient of oxygen as $-0{\cdot}000964$ (GRAY and BURT), then the ratio of the volumes containing equal numbers of molecules at N.T.P. is $\dfrac{1+0{\cdot}00054}{1-0{\cdot}000964}$ and the ratio of the combining volumes $\dfrac{2\,(1+0{\cdot}00054)}{1-0{\cdot}000964} = 2{\cdot}00303$.

Purity of the Gases.

Provided that the source of the gas and the methods of purification are varied, the best criterion of purity is afforded by the concordance of the results.

Neither of the gases, in the condition in which they left the trains, yielded any residue when pumped through a spiral cooled in liquid air.

The liquefied oxygen left no residue on evaporation, and the results did not vary according to the fraction taken. Nitrogen might occur as an impurity owing to incomplete exhaustion of the trains, or to a faulty tap. In the first case the quantity would diminish throughout a series and, since the resulting error would not be constant, it could hardly escape detection. The taps on the apparatus were selected with great care. They were mounted on capillary tube, and, in the case of the 3-way taps, had the two bores drilled diagonally and at right angles to each other. Experience has shown this to be the safest type for preventing leak. All taps through which gas passed were mercury cupped. The plugs were so finely ground that a very small quantity of grease sufficed to lubricate them, and they were kept well " home " in their barrels by means of rubber bands. When in use, the plug was turned through the smallest possible arc, a precaution which tends to prevent the appearance of striæ, particularly when the tap is in service for a long time. The grease used was the well-known rubber-paraffin-vaseline mixture, and, contrary to the experience of GERMANN(13), we found that oxygen had no detectable effect on its appearance or properties. No leak between the interior of the apparatus and the air was ever observed, though the point was frequently tested. Nitrogen was tested for directly by exploding down about 1200 c.c., of hydrogen and 600 c.c. of oxygen, the quantities being adjusted so that hydrogen was in slight excess. The hydrogen residue, of about 3 c.c., was transferred to a small explosion eudiometer and mixed with 2 c.c. of oxygen. After passing a spark and introducing a small quantity of alkaline pyrogallol solution, about 1 c.mm. of gas remained unabsorbed. In other experiments hydrogen and oxygen residues were sparked over water or potash ; in no case was any diminution in volume noticed.

The presence of nitrogen in either gas might give rise to traces of oxides of nitrogen, and eventually nitric acid, as a result of the explosions, or to ammonia as a result of the sparking. Oxides of nitrogen (except nitric oxide), nitric acid, and ammonia would remain with the ice in the explosion vessel. The water formed left no residue on the glass or mercury surfaces when evaporated; was odourless, tasteless, and neutral in re-action, and, when tested for nitric acid and ammonia, gave negative results. Traces of nitrogen, or other gases, in the hydrogen, provided that they were left unaltered by the explosions and sparking, would introduce no error, since they would be measured as part of the hydrogen residue. Any such impurity in the oxygen, on the other hand, would make the hydrogen residue too great by an amount equal to three times the volume of the original impurity.

The presence of carbon compounds in either gas would almost certainly lead to the formation of carbon dioxide in the explosion vessel. Since the vapour pressure of carbon dioxide, at the temperature of the acetone, solid carbon dioxide mixture used for freezing out the water, is more than 40 mm. of mercury, this gas would escape with the hydrogen from the explosion vessel to be retained and detected in the liquid-air-cooled spiral.

We have no direct proof of the completeness of synthesis, but the hydrogen residues were sparked at different pressures and for varying periods of time without affecting the results. The measured volume of hydrogen left in the pipette at the end of a determination was usually removed by the mercury pump, but in experiments 7, 8 and 9 of series 4, it was transferred to the explosion vessel and constituted the first hydrogen filling of the succeeding experiment.* The results show no indication of an accumulating impurity.

The successful removal of water from the hydrogen residue was proved by the fact that the small phosphoric oxide tube between the explosion vessel and the pump showed no signs of deliquescence after four years' use.

Accuracy of Volume, Pressure, and Temperature Measurements.

Owing to the fact that all gas measurements were made in the same vessel under the same conditions, various possible errors in this category tend to cancel out.

Volume errors.—Since all volumes were measured in terms of a weight of mercury, an accuracy greater than necessary was readily secured. The only operation in which special care was needed to prevent a volume error was the setting of the meniscus to the point in the dead-space. The final adjustment was always made with a rising meniscus, and cohesion effects were minimised by tapping the glass or pinching the reservoir tubing. The probable limits of variation may be estimated from the concordance of the values obtained in calibrating the dead-space at the beginning of the research.

Pressure errors.—The vertical distance between the two glass points of the manometer was measured with a cathetometer when the system was in ice. The accuracy attainable was not very great because of distortion by the small bath round the dead-space, but from two measurements giving values 760·35 and 760·32 mm., respectively, it may be concluded that the distance was within a third of a millimetre of the normal barometric height. A deviation of 1 mm. alters the density ratio only by 1 part in 500,000, so that a difference of the above order is quite negligible.

The precision with which the mercury meniscuses could be set to the two points was certainly very high. The order of accuracy attainable was tested in the following way: the upper chamber of the manometer was viewed through a telescope fitted with a Hilger micrometer eye-piece, and the cross-wire was set on the point. The meniscus was then adjusted until the cross-wire appeared exactly tangential to it. On examination with the pocket lens which was used in making the settings, a distinct gap was detectable between the point and its mirror image. Assuming the limit of accuracy with a micrometer to be 0·01 mm., it was estimated that adjustment by means of the lens should be within 0·002 mm.

The effect of capillarity on the pressure measurement can be neglected, since in tubes of the diameter of the point chambers (16 mm.), even the absolute depressions are vanishingly small.

Temperature errors.—These were undoubtedly the limiting factors in the accuracy of the work. Several have already been discussed in detail in the course

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* At this stage of the research the bubble trapped in the dead-space was removed after expulsion of each pipette-full of gas, so that the final hydrogen filling was not contaminated with oxygen.

of the paper. They may be tabulated here conveniently under five heads, as errors due to :—

(1) Length of time required for the gas in the pipette to cool to 0° C.
(2) Variation in the temperature of the iced system on different occasions.
(3) Rise in temperature in parts of the iced system before completion of setting.
(4) Variation in temperature of exposed portion of manometer column.
(5) Relative temperature change in the mercury in the manometer and dead-space below the level of the point.

Comment on the nature of the error under each head may be made as follows :—

(1) Systematic error, which was estimated in the first four series and eliminated in the fifth.

(2) Probably very small errors : the point was frequently tested by repeating a measurement on the following day, when results agreeing to within a few cubic millimetres could be obtained, provided that the pipette had been in ice for a sufficient length of time.

(3) Negligible errors : experiments prove that the system remained at 0° C. for a much longer period than was actually required for the setting.

(4) Small hap-hazard errors, estimated and corrected for in series 3 and 4 and eliminated in series 5.

(5) Small hap-hazard errors, except perhaps in series 5.

A very large proportion of the time occupied by this research was spent in investigating errors of temperatures and, although we have no reason to regard our final result as seriously affected by such errors, we are inclined to believe that if the whole of the measuring apparatus down to the point where the manometer joins the tubing below the dead-space had been in direct contact with melting ice, a better concordance would have been obtained.

One further point suggested itself as worth examination. With the measuring apparatus used only a small variation was possible in the volume of hydrogen taken for synthesis. In the first three series, where this variation was greatest, there is no indication of any connection between the quantity of hydrogen taken and the result. Of the thirty-two experiments considered, the mean of those sixteen in which the hydrogen excess was greatest agrees to 1 part in 100,000 with the mean of the other sixteen.

The Atomic Weight of Hydrogen.

If the ratio of the combining volumes is 2·00288 the atomic weight of hydrogen is 1·00772, when MORLEY's values for the densities, namely, 0·089873 and 1·42900, are taken

Comparing our result with those of MORLEY and NOYES, we have :—

MORLEY	1·00762,
NOYES.	1·00787,

or, as estimated by CLARKE from the same data,

	1·00783,
BURT and EDGAR .	1·00772.

Our value, therefore, is very nearly the arithmetic mean of the other two.

In 1914, a paper was published by GERMANN(14) containing a series of measurements of the density of oxygen.

As a mean of fifteen experiments he obtained the value 1·42906 for the weight of a normal litre. The gas was made by heating potassium permanganate, and, after passing over potash and phosphoric oxide, was liquefied and fractionated. This last precaution entitles his results to special consideration. Collecting the results obtained by MORLEY, RAYLEIGH, and GERMANN, we have :—

MORLEY (41 experiments)	1·42900
RAYLEIGH (16 experiments) . . .	1·42904
GERMANN (15 experiments) . . .	1·42906.

The arithmetic mean is 1·42903, but GERMANN, attaching rather greater weight to his own result, partly because his oxygen was liquefied and fractionated, and partly because of special precautions taken in measuring the pressure, proposes the figure 1·42905 as the most probable value on existing data. Further confirmation of the higher value is afforded by the work of SCHEUER(15), who has recently obtained a result identical with GERMANN'S. The substitution of this value (1·42905) for MORLEY'S in the density ratio alters our atomic weight to 1·00769. It seems unlikely that any probable future alteration in the density ratio would bring our value as low as MORLEY'S or as high as NOYES', and we may conclude that the true value of the atomic weight of hydrogen lies very close to

1·0077.

Part of the expense of this work was defrayed by a Royal Society Grant which we desire to acknowledge here. We are indebted to Prof. DIXON for his continued interest in the research and for a number of helpful suggestions.

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SERIES A, VOL. 216. Pp. 429–457.

[PLATE 1.]

MATHEMATICAL CONTRIBUTIONS TO THE THEORY OF EVOLUTION.

XIX. SECOND SUPPLEMENT TO A MEMOIR ON SKEW VARIATION.

BY

KARL PEARSON, F.R.S.

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IX. *Mathematical Contributions to the Theory of Evolution.—XIX. Second Supplement to a Memoir on Skew Variation.*

By KARL PEARSON, *F.R.S.*

Received February 2,—Read February 24, 1916.

[PLATE 1.]

(1) IN a memoir presented to the Royal Society in 1894, I dealt with skew variation in homogeneous material. The object of that memoir was to obtain a series of curves such that one or other of them would agree with any observational or theoretical frequency curve of positive ordinates to the following extent:—(i) The areas should be equal; (ii) the mean abscissa or centroid vertical should be the same for the two curves; (iii) the standard deviation (or, what amounts to the same thing, the second moment coefficient) about this centroid vertical should be the same, and (iv) to (v) the third and fourth moment coefficients should also be the same. If μ_s be the s^{th} moment coefficient about the mean vertical, N the area, $\bar{x}$ be the mean abscissa, $\sigma = \sqrt{\mu_2}$ the standard deviation, $\beta_1 = \mu_3^2/\mu_2^3$, $\beta_4 = \mu_4/\mu_2^2$, then the equality for the two curves of N, $\bar{x}$, σ, β_1 and β_2 leads almost invariably in the case of frequency to excellency of fit. Indeed, badness of fit generally arises from either heterogeniety, or the difficulty in certain cases of accurately determining from the data provided the true values of the moment coefficients, *e.g.*, especially in J- and U-shaped frequency distributions, or distributions without high contact at the terminals; here the usual method of correcting the raw moments for sub-ranges of record fails.

Having found a curve which corresponded to the skew binomial in the same manner as the normal curve of errors to the symmetrical binomial with finite index, it occurred to me that a development of the process applied to the hypergeometrical series would achieve the result I was in search of, *i.e.*, a curve whose constants would be determined by the observational values of N, $\bar{x}$, σ, β_1 and β_2.

The hypergeometrical series was one not only arising naturally in chance problems, but covering in itself a most extensive range of functions. The direct advantage of the hypergeometrical series is that it abrogates the fundamental axioms on which the Gaussian frequency is based. The equality in frequency of plus and minus errors of the same magnitude is replaced by an arbitrary ratio, the number of contributory

[Published June 6, 1916.

causes is no longer indefinitely large, and the contributions of these causes are no longer independent but correlated.*

Since β_1 and β_2 are by nature positive we can represent all possible values of β_1 on a chart in which β_1 and β_2 are the co-ordinates of a point in the positive quadrant. But a little consideration shows that β_2 must be greater than β_1, thus one-half the area of the quadrant, that above the line $\beta_2 = \beta_1$ is removed from the field of possible occurrences. Further, there is a limit to the application of the series of curves discussed when β_2 gets large, for the high moments of two of the types of curves, *i.e.*, Types IV. and VI., or

$$y = y_0 \frac{e^{-\nu \tan^{-1} x/a}}{\left(1+\frac{x^2}{a^2}\right)^{\frac{1}{2}(r+2)}} \quad \text{and} \quad y = y_0 \frac{(x-a)^{q_2}}{x^{q_1}},$$

become infinite when the order of the moment is greater than r, or the probable error of the fourth moment would become indefinitely large for $r = 7$, *i.e.*, we are practically limited by the line $8\beta_2 - 15\beta_1 - 36 = 0$. The first four moments of the curve remain finite, but from the fifth onwards they can become infinite, the lines corresponding to these, however, lying outside the above line.† For curves corresponding to points below this line it is fitting to take as differential equation

$$\frac{1}{y}\frac{dy}{dx} = \frac{b+x}{c_0+c_1x+c_2x^2+c_3x^3}, \quad \ldots \ldots \ldots \quad \text{(i)}$$

or a slightly more general form which is related to the higher hypergeometrical $F(\alpha, \beta, \gamma, \theta, \epsilon, 1)$ as the present series of curves to the simple hypergeometrical $F(\alpha, \beta, \gamma, 1)$. The whole theory of curves of the above type has been worked out for some time past, but has remained unpublished, for we failed to find any definitely homogeneous data by which it could be effectively illustrated, and for this reason *heterotypic* curves have for the time being been left in abeyance. We may, however, notice the following point. If we take our generalised hypergeometrical to be

$$1 + \frac{\alpha \, . \, \beta \, . \, \gamma}{\theta \, . \, \epsilon \, . \, \zeta} + \frac{(\alpha+1)(\beta+1)(\gamma+1)\,\alpha \, . \, \beta \, . \, \gamma}{(\theta+1)(\epsilon+1)(\zeta+1)\,\theta \, . \, \eta \, . \, \zeta} + \ldots$$

$$= y_0 + y_1 + y_2 + \ldots .$$

Then

$$\frac{y_{x+1}}{y_x} = \frac{(\alpha+x)(\beta+x)(\gamma+x)}{(\theta+x)(\epsilon+x)(\zeta+x)},$$

and this will correspond to the ordinary form if $\zeta = 0$, *i.e.*, $F(\alpha, \beta, \gamma, \theta, \epsilon, 1)$.

---

* Just as values of the binomial $(p+q)^n$ with negative n and $p > 1$ very often give good fits to frequency distributions, so we have recently found that hypergeometricals $F(\alpha, \beta, \gamma, 1)$ with imaginary α and β are of fairly common occurrence in frequency distributions, and when applied to individual samples from real hypergeometrical populations may give better fits than the theoretical series, *i.e.*, in card drawings.

† See RHIND, 'Biometrika,' vol. VII., p. 133.

We have

$$\frac{y_{x+1}-y_x}{\frac{1}{2}(y_{x+1}+y_x)} = \frac{2\{\alpha\beta\gamma-\theta\epsilon\xi+x(\alpha\beta+\beta\gamma+\gamma\alpha-\theta\epsilon-\epsilon\xi-\xi\theta)+x^2(\alpha+\beta+\gamma-\theta-\epsilon-\xi)\}}{\{\alpha\beta\gamma+\theta\epsilon\xi+x(\alpha\beta+\beta\gamma+\gamma\alpha+\theta\epsilon+\epsilon\xi+\xi\theta)+x^2(\alpha+\beta+\gamma+\theta+\epsilon+\xi)+2x^3\}},$$

and accordingly we get the curve approximating to the hypergeometrical of the higher order by putting

$$\frac{1}{y}\frac{dy}{dx} = \frac{\text{quadratic function of } x}{\text{cubic function of } x},$$

$$= \frac{a_0+a_1x+a_2x^2}{c_0+c_1x+c_2x^2+c_3x^3}, \quad \ldots\ldots\ldots\ldots \quad \text{(ii)}$$

where the six independent constants can be expressed in terms of the original six, α, β, γ, θ, ϵ, ξ. It will be seen that a hypergeometrical of the second order will, in general, have *two* modes, the exception being when

$$\alpha+\beta+\gamma = \theta+\epsilon+\xi; \quad \ldots\ldots\ldots\ldots \quad \text{(iii)}$$

in which case (ii) coincides with (i) the general equation to the fourth approximation of curves when β_1 and β_2 fall into the heterotypic area. It will thus be noted that such curves approximate to hypergeometric series of the second order when the special condition (iii) holds; always assuming the unimodal character of homogeneous material. It seems probable that for the most part bimodal frequencies would be those that lead to values of β_1 and β_2 lying in the heterotypic region, and such are excluded from practical statistics.

In the original paper* four types of curves were dealt with beside the Gaussian curve corresponding to an isolated point. A supplementary memoir issued in 1901† dealt with two further types, which had been overlooked until actual experience demonstrated their existence. I have now to confess the omission of five further types, not to speak of a horizontal straight line, as sub-groups of the J-section of curves, which are themselves in practice so rare, that the region of the β_1, β_2 plane in which they occur had not been very fully investigated. My attention was drawn to these curves while considering the frequency curves for the correlation of small samples. If we take a sample of four from uncorrelated material, the sample is equally likely to have every correlation from -1 to $+1$.‡ In this case, $\beta_1 = 0$, $\beta_2 = 1{\cdot}8$, and the frequency curve is a horizontal straight line. What would my series of curves give in this case? I discovered that they also gave a rectangle of frequency or a horizontal straight line, and this discovery led me to a closer investigation of the sub-groups of curves in the neighbourhood of the J-curve area. The point in the

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* 'Phil. Trans.,' A, vol. 186 (1895), pp. 343–414.

† 'Phil. Trans.,' A, vol. 196 (1901), pp. 443–459.

‡ 'Biometrika,' vol. VI., p. 306, and vol. X., p. 312.

$\beta_1\,\beta_2$ plane for which $\beta_1 = 0$, $\beta_2 = 1{\cdot}8$, I term the *rectangle-point* and denote by R. (See folding diagram, Plate 1, at end of paper.)

The rectangle-point is the point of contact with the axis of β_2 of the biquadratic

$$\beta_1\,(8\beta_2-9\beta_1-12)\,(\beta_2+3)^2 = (4\beta_2-3\beta_1)\,(10\beta_2-12\beta_1-18)^2,$$

which bounds the area of J-curves. The novel curves are in part limiting curves which occur when the point β_1, β_2 lies on this biquadratic, *i.e.*, transition curves from J-curves to U-curves and from J-curves to limited range curves, and in part a limiting curve which exists along the line $5\beta_2-6\beta_1-9 = 0$ which passes through the rectangular point and never again meets the biquadratic in the loop in the positive quadrant. It would be convenient to speak of this line as the axis of the biquadratic loop, but unfortunately the loop is not symmetrical about it, and to avoid misunderstanding I term it the R-line.

Up to the present the minimum limit to the area of U-curves had not been given. Since β_2 is $> \beta_1$, half the positive quadrant was impossible, but a recent observation shows that frequency curves above the line $\beta_2-\beta_1-1 = 0$ are impossible. This limit was suggested in the following manner. When samples of three are taken from an indefinite population, the frequency curves for the correlation of any two variates of the three individuals sampled are U-shaped frequency curves, but when samples of two are taken the correlation must be either positive or negative, and accordingly the frequency is collected into two lumps or blocks as a limiting case of a U-shaped distribution. But for two such lumps $\beta_2-\beta_1-1 = 0$. In other words, along the line $\beta_2-\beta_1-1 = 0$, the U-shaped frequency either brings all frequency to an end, or passes through a transitional case. The former is the true state of affairs, for β_2 cannot be less than β_1+1. To demonstrate this,[*] let $s_p = \mathrm{S}\,(x_n{}^p)$, and let there be n quantities x_u. Clearly, $s_0 = n$, and $s_1 = 0$. Now by BURNSIDE and PANTON, 'Theory of Equations,' vol. II., p. 35,

$$\sum_{\substack{r>s>t\\ r,\,s,\,t=1}}^{n} \{(x_s-x_t)^2\,(x_t-x_r)^2\,(x_r-x_s)^2\} = \begin{vmatrix} s_0, & s_1, & s_2 \\ s_1, & s_2, & s_3 \\ s_2, & s_3, & s_4 \end{vmatrix}$$

$$= \begin{vmatrix} n, & 0, & s_2 \\ 0, & s_2, & s_3 \\ s_2, & s_3, & s_4 \end{vmatrix} = n\,(s_2s_4-s_3{}^2) - s_2{}^3$$

$$= s_2{}^3\left(\frac{s_4/n}{s_2{}^2/n^2} - \frac{s_3{}^2/n^2}{s_2{}^3/n^3} - 1\right) = s_2{}^3\left(\frac{\mu_4}{\mu_2{}^2} - \frac{\mu_3{}^2}{\mu_2{}^3} - 1\right)$$

$$= s_2{}^3\,(\beta_2-\beta_1-1),$$

---

[*] I owe this neat proof to the kindness of Mr. G. N. WATSON.

which must therefore be either zero or a positive quantity. Thus we see that the whole area covered by my frequency curves is limited above by the line $\beta_2-\beta_1-1=0$, and below by the line $8\beta_2-15\beta_1-36=0$. The first line limits all frequency; the second line limits my types.*

(2) Before proceeding further, let us examine the limit to all frequency. Consider the line $\beta_2-\beta_1-1=0$.

The form of the curve is†

$$y=y_0\left(1+\frac{x}{a_1}\right)^{m_1}\left(1-\frac{x}{a_2}\right)^{m_2}.$$

Now,

$$m'^2-rm'+\epsilon=0,$$

where

$$r=\frac{6(\beta_2-\beta_1-1)}{3\beta_1-2\beta_2+6},$$

therefore

$$r=0 \quad\text{and}\quad \epsilon=\tfrac{1}{4}r^2/(1-\kappa_2)\text{ also }=0.$$

Hence

$$m'_1+m'_2=0 \text{ and } m'_1m'_2=0, \quad\text{or}\quad m_1=-1,\ m_2=-1.$$

The form of the curve is accordingly

$$y=\frac{y_0}{\left(1+\frac{x}{a_1}\right)\left(1-\frac{x}{a_2}\right)},$$

or, apparently, U-shaped. Now

$$\begin{aligned} b &= \tfrac{1}{2}\sigma\left\{\beta_1(r+2)^2+16(r+1)\right\}^{1/2} \\ &= \sigma\left\{\beta_1+4\right\}^{1/2}, \end{aligned}$$

and is finite. But

$$\begin{aligned} y_0 &= \frac{\mathrm{N}}{b}\,\frac{m_1{}^{m_1}m_2{}^{m_2}}{(m_1+m_2)^{m_1+m_2}}\,\frac{\Gamma(m_1+m_2+2)}{\Gamma(m_1+1)\,\Gamma(m_2+1)}, \\ &= \frac{\mathrm{N}}{b}\,\frac{(m_1+1)(m_2+1)}{m_1+m_2+2}\,\frac{m_1{}^{m_1}m_2{}^{m_2}}{(m_1+m_2)^{m_1+m_2}}\,\frac{(m_1+2)(m_2+2)}{(m_1+m_2+3)}\times\frac{\Gamma(m_1+m_2+4)}{\Gamma(m_1+3)\times\Gamma(m_2+3)}, \\ &= \frac{\mathrm{N}}{b}\text{ limit of }\frac{(m_1+1)(m_2+1)}{m_1+m_2+2}\,\frac{4\times\Gamma(2)}{\Gamma(2)\times\Gamma(2)}. \end{aligned}$$

But

$$\text{limit of }\frac{(m_1+1)(m_2+1)}{m_1+m_2+2}=\frac{\lambda_1\lambda_2}{\lambda_1+\lambda_2},$$

---

* It is not accurately correct to say it limits my types of skew curves. What it actually does is to cut off an area in which the probable errors of the constants of Types IV. and VI. curves can be very great. The curves may give a good fit, but the constants cannot be cited as characteristics of the frequency distribution as they are unstable.

† The notation throughout is that of my original 'Phil. Trans.' memoirs of 1895 and 1901.

when both $\lambda_1\lambda_2$ are to be made vanishingly small, being m_1+1 and m_2+1 respectively. Thus the limit

$$= \frac{1}{1/\lambda_1+1/\lambda_2} = \frac{1}{\infty} = 0.$$

Hence y_0 vanishes or y is zero at all points, but $x = -a_1$ and $x = a_2$ where it is undetermined.

Since $m_1/a_1 = m_2/a_2$, we have $a_1 = a_2$, and the frequency really consists of two concentrated groups at $-a_1$ and a_2, or at $\pm\frac{1}{2}b$.

If μ'_1 and μ''_1 be the distances of the centroid from the two ends of the range,

$$\frac{\mu'_1}{\mu''_1} = \frac{n''}{n'},$$

where n' and n'' are the frequencies concentrated at the range terminals. But $\mu'_1 = b\,(m_1+1)/(m_1+m_2+2)$, or we have $\mu'_1/\mu''_1 = (m_1+1)/(m_2+1) = \lambda_1/\lambda_2$, or is the finite quantity which marks the ratio of the vanishing of m_1+1 and m_2+1 ; this, therefore, is equal to n''/n'.

Clearly

$$\mu'_1 = (n''-n')/(n''+n')\,\frac{b}{2},$$

$$\mu'_2 = (n''+n')/(n''+n')\,\frac{b^2}{4} = \tfrac{1}{4}b^2,$$

$$\mu'_3 = (n''-n')/(n''+n')\,\frac{b^3}{8},$$

$$\mu'_4 = (n''+n')/(n''+n')\,\frac{b^4}{16} = \tfrac{1}{16}b^4,$$

and

$$\mu_2 = b^2\,(n'n'')/(n'+n'')^2,$$

$$\mu_3 = b^3n'n''(n''-n')/(n'+n'')^3,$$

$$\mu_4 = b^4n'n''\,(n'^2+n''^2-n'n'')/(n'+n'')^4.$$

Thus

$$\beta_1 = \frac{n''}{n'}+\frac{n'}{n''}-2, \quad \beta_2 = \frac{n''}{n'}+\frac{n'}{n''}-1,$$

giving as verification $\beta_2-\beta_1-1 = 0$.

Thus the whole problem is solved if we know the magnitude of the two frequencies n' and n'' concentrated at $-\frac{1}{2}b$ and $+\frac{1}{2}b$.

As special cases the point on the β_2-axis gives $\beta_1 = 0$, $\beta_2 = 1$, and represents two equal concentrated frequency lumps $n' = n'' = \frac{1}{2}\mathrm{N}$. The point at ∞ on the line $\beta_2-\beta_1-1 = 0$, or $\beta_1 = \beta_2 = \infty$ represents a single frequency lump, for which $n' = 0$, $n'' = \mathrm{N}$. I speak of these concentrated frequency lumps lying on the line $\beta_1-\beta_2-1 = 0$, as block-frequency, and represent them by the letter B; they correspond to points on the B-line. (See Diagram, Plate 1.)

The most remarkable limiting case of this kind has been already referred to. It will be shown in practical examples in a memoir on "small samples," now nearly ready for press, that the correlation between two variates may be determined by sampling these populations in pairs, and merely observing, which can be usually done without measurement, whether the pair is positively or negatively correlated. The ratio of the two frequency "lumps" easily provides the correlation.*

(3) Let us now consider the nature of the frequency on the loop of the biquadratic. Taking the form of the curve to be

$$y = y_0 (1+x/a_1)^{m_1} (1-x/a_2)^{m_2}$$

we know that m_1 and m_2 are the roots of the quadratic

$$m^2-m(r-2)+\epsilon-r+1 = 0,$$

where

$$r = 6(\beta_2-\beta_1-1)/(3\beta_1-2\beta_2+6),$$

and

$$\epsilon = \frac{r^2}{4+\frac{1}{4}\beta_1(r+2)^2/(r+1)}.$$

Now $\epsilon-r+1 = 0$ provides the biquadratic

$$\beta_1(8\beta_2-9\beta_1-12)(\beta_2+3)^2-(10\beta_2-12\beta_1-18)^2(4\beta_2-3\beta_1) = 0;$$

actually

$$\epsilon-r+1 = \frac{(4\beta_2-3\beta_1)(10\beta_2-12\beta_1-18)^2-\beta_1(\beta_2+3)^2(8\beta_2-9\beta_1-12)}{(3\beta_1-2\beta_2+6)\{\beta_1(\beta_2+3)^2+4\beta_1(4\beta_2-3\beta_1)(3\beta_1-2\beta_2+6)\}}.$$

Now β_1, $4\beta_2-3\beta_1$ and β_2+3 are by their nature essentially positive. Hence, provided $3\beta_1-2\beta_2+6$ is positive, *i.e.*, as long as we deal with points above the line $2\beta_2-3\beta_1-6 = 0$, *i.e.*, the Type III. curve line, $\epsilon-r+1$ will be positive, if (β_1, β_2) lie outside the loop of the biquadratic. But within the loop it is negative, or one value of m must be negative, or we reach an infinite ordinate at $x = -a_1$ or a_2, *i.e.*, a J-shaped curve. The other ordinate at $x = a_2$ or $-a_1$ is zero, because the other m must be a finite positive quantity.

If $\epsilon-r+1 = 0$, *i.e.*, along the biquadratic loop, one value of m is zero, and the other is positive if r be greater than 2, and negative if it be less than 2. But

$$r-2 = \frac{2(5\beta_2-6\beta_1-9)}{3\beta_1-2\beta_2+6}.$$

Accordingly above the line $5\beta_2-6\beta_1-9 = 0$, and above the line $2\beta_2-3\beta_1-6 = 0$, $r-2$ will be negative, but these lines do not meet in the positive quadrant. Hence all

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* See "STUDENT," 'Biometrika,' vol. VI., p. 304, and FISHER, 'Biometrika,' vol. X., p. 508.

along the upper boundary of the loop one m is zero and the other negative. Accordingly, from the R-point round the upper boundary of the loop, we have the curve

$$y = y_0 (1+x/a_1)^{-m'_1}.$$

I call this curve Type VIII.

Since $-m'_1/a_1 = m_2/a_2$, and m_2 is zero while m_1 and a_1 are finite, it follows that $a_2 = 0$, and accordingly the range of frequency is from $x = 0$ to $x = -a_1$. The curve is therefore a J-shaped curve with infinite ordinate at one end of the range and a finite ordinate at the other.

Now consider the lower side of the loop. Here $5\beta_2-6\beta_1-9$ will be positive, for this side is below the R-line and $3\beta_1-2\beta_2+6$ will also be positive until the point in which the line $2\beta_2-3\beta_1-6 = 0$ meets the lower side of the loop, *i.e.*, the point $\beta_1 = 4$, $\beta_2 = 9$. Hence from the R-point up to $\beta_1 = 4$, $\beta_2 = 9$, a point practically outside the range of the customary statistical frequencies, $r-2$ will be positive, or m_1 will be positive. Further m_1 and a_1 being finite and m_2 zero, it follows that a_2 is zero, or the curve is

$$y = y_0 (1+x/a_1)^{m_1}.$$

In this case the curve has a zero ordinate at one end and a finite ordinate at the other. I term this curve Type IX.

At the point where the line $2\beta_2-3\beta_1-6 = 0$ meets the biquadratic, Type IX. agrees with my earlier Type III.

The equation to that type is*

$$y = y_0 (1+x/a)^{\gamma a} e^{-\gamma x},$$

where

$$\gamma a = \frac{4}{\beta_1} - 1 \quad \text{and} \quad \gamma = \frac{2}{\sigma\sqrt{\beta_1}}.$$

Hence for $\beta_1 = 4$, $\gamma a = 0$, and $\gamma = 1/\sigma$. Thus a is zero and the curve becomes

$$y = y_0 e^{-x/\sigma},$$

the range being from 0 to ∞.

But in Type IX., since r has become infinite, m_1 is infinite and the limit to

$$y = y_0 (1+x/a_1)^{m_1}$$

is accordingly the exponential curve

$$y = y_0 e^{-\lambda x},$$

as we shall see shortly λ must equal $1/\sigma$, where σ is the standard deviation.

I propose to call this exponential curve Type X., and the point $\beta_1 = 4$, $\beta_2 = 9$, E or the exponential point.

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[*] 'Phil. Trans.,' A, vol. 186, p. 373.

Beyond the exponential point, our biquadratic branch has entered the area of Type VI. curves,[*] and m_1 will now again be negative.

Now the equation to Type VI. is

$$y = y_0 \frac{(x-a)^{q_2}}{x^{q_1}},$$

and the range from $x = a$ to ∞. The special case of this along the branch of the biquadratic occurs when $q_2 = 0$, leading to[†]

$$1 - q_1 = \epsilon_1 = r - 1,$$

or

$$y = y_0/x^{q_1}$$

where

$$q_1 = \frac{2(5\beta_2 - 6\beta_1 - 9)}{2\beta_2 - 3\beta_1 - 6},$$

which is positive, since q_1 is now beneath both the lines

$$5\beta_2 - 6\beta_1 - 9 = 0 \quad \text{and} \quad 2\beta_2 - 3\beta_1 - 6 = 0.\text{[‡]}$$

This curve, which will be more fully considered below, has a range from a certain value a to ∞. It thus starts with a finite ordinate and asymptotes to zero. It is a transition curve extending from the exponential point along the lower limb of the biquadratic loop. I call this curve Type XI. The biquadratic never cuts the cubic along which Type V. lies and no further change occurs in Type XI.

I now pass to the consideration of the R-line or $5\beta_2 - 6\beta_1 - 9 = 0$.

The general differential equation[§] to the type of frequency curve under consideration is

$$\frac{1}{y}\frac{dy}{dx} = \frac{-\{\sqrt{\beta_1}(\beta_2+3) + (10\beta_2 - 12\beta_1 - 18)\,x/\sigma\}}{\sigma\{4\beta_2 - 3\beta_1) + \sqrt{\beta_1}(\beta_2+3)\,x/\sigma + (2\beta_2 - 3\beta_1 - 6)\,x^2/\sigma^2\}},$$

the origin being *at the mean*.

Hence if $5\beta_2 - 6\beta_1 - 9 = 0$, the term in x/σ disappears from the numerator, and we can further get rid of β_2 by substituting $\frac{1}{5}(6\beta_1 + 9)$ for it. Making this substitution, we reach

$$\frac{1}{y}\frac{dy}{dx} = \frac{-2\sqrt{\beta_1}}{\sigma(3+\beta_1) - \sigma(\sqrt{\beta_1} - x/\sigma)^2}.$$

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[*] 'Phil. Trans.,' A, vol. 197, p. 449.

[†] *Loc. cit.*, Equations, bottom of p. 449.

[‡] As we pass outwards from the exponential point along the biquadratic q_1 ranges from ∞ to 5, which it reaches at the asymptote to the biquadratic $\beta_1 = 50$, or when $\beta_2 = \infty$, $\beta_1 = 50$.

[§] "Mathematical Contributions to the Theory of Evolution, XIV. On the General Theory of Skew Correlation and Non-Linear Regression," p. 6, 'Drapers' Company Research Memoirs,' Cambridge University Press.

This leads on integration to

$$y = y_0 \left(\frac{\sigma(\sqrt{3+\beta_1}+\sqrt{\beta_1})+x}{\sigma(\sqrt{3+\beta_1}-\sqrt{\beta_1})-x} \right)^{\sqrt{\frac{\beta_1}{3+\beta_1}}}.$$

I term this Type XII., or the R-line J-curve. The origin is the mean, the range from $x = -\sigma(\sqrt{3+\beta_1}+\sqrt{\beta_1})$ to $\sigma(\sqrt{3+\beta_1}-\sqrt{\beta_1})$. It separates J-curves—so long as we are above the line $2\beta_2-3\beta_1-6 = 0$—for which $r-2$ is positive from those in which $r-2$ is negative. But $r-2 = m_1+m_2$. Hence below the R-line the positive m_1 is greater than the negative m_2, but above this line the positive m_1 is less than the negative m_2, *i.e.*, the upright of the J is emphasised at the expense of the horizontal part, while below the R-line this condition is reversed until on the biquadratic the infinite ordinate of the J-upright is replaced by a finite ordinate.

I propose now to consider a little in detail the nature of these new types of frequency and the manner of fitting them to actual data. I have dealt above sufficiently fully with "block-frequency" and its criterion $\beta_2-\beta_1-1 = 0$ and therefore need only consider Types VIII. to XII.

(4) *Frequency Curve. Type VIII.*—

$$y = y_0(1+x/a)^{-m}.$$

Range, from $x = 0$ to $x = -a$.*

y_0 is clearly the value of the ordinate at $x = 0$, *i.e.*, the finite ordinate at the tail.

We easily deduce if N be the total frequency $y_0 = \mathrm{N}(1-m)/a$, and taking the origin at $x = -a$,

$$\bar{x} = \mu'_1 = a(1-m)/(2-m), \qquad \mu'_2 = a^2(1-m)/(3-m),$$
$$\mu'_3 = a^3(1-m)/(4-m), \qquad \mu'_4 = a^4(1-m)/(5-m).$$

Hence for the moment-coefficients about the mean

$$\sigma^2 = \mu_2 = a^2(1-m)/\{(3-m)(2-m)^2\},$$

$$\mu_3 = 2a^3m(1-m)/\{(4-m)(3-m)(2-m)^3\},$$

$$\mu_4 = 3a^4(1-m)(4-5m+3m^2)/\{(5-m)(4-m)(3-m)(2-m)^4\}.$$

These lead to

$$\beta_1 = \frac{4m^2(3-m)}{(1-m)(4-m)^2}, \qquad \beta_2 = \frac{3(3-m)(4-5m+3m^2)}{(1-m)(4-m)(5-m)}.$$

Clearly m could be found from the value of β_1 by solving the cubic equation

$$m^3(4-\beta_1)+m^2(9\beta_1-12)-24\beta_1 m+16\beta_1 = 0.$$

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* Of course, whether a is really positive or negative will depend on the sign given to x, or the direction of the x-axis.

then a is determined from

$$a = \pm\sigma(2-m)\sqrt{\frac{3-m}{1-m}},$$

the sign being determinable from the observed value of μ_3 and y_0 from

$$y_0 = \frac{N(1-m)}{a} = \frac{N}{\sigma}\frac{1-m}{2-m}\sqrt{\frac{1-m}{3-m}},$$

and the placing of the frequency curve on the observations by

$$\mu'_1 = a(1-m)/(2-m).$$

If, however, we find $10\beta_2-12\beta_1-18$ and $3\beta_1-2\beta_2+6$, we have

$$10\beta_2-12\beta_1-18 = +\frac{24m(m-2)^3}{(1-m)(5-m)(4-m)^2},$$

$$3\beta_1-2\beta_2+6 = -\frac{24(m-2)^3}{(1-m)(5-m)(4-m)^2},$$

giving

$$m = -\frac{2(5\beta_2-6\beta_1-9)}{3\beta_1-2\beta_2+6},$$

and thus since m is to be positive, the point (β_1, β_2) must be *above* the line $5\beta_2-6\beta_1-9 = 0$. The line $2\beta_2-3\beta_1-6 = 0$ does not meet $5\beta_2-6\beta_1-9 = 0$ in the positive quadrant, so that a point below both these lines does not exist in real frequency. Clearly

$$1-m = (8\beta_2-9\beta_1-12)/(3\beta_1-2\beta_2+6),$$
$$3-m = (4\beta_2-3\beta_1)/(3\beta_1-2\beta_2+6),$$
$$4-m = 2(\beta_2+3),$$

and thus if these values be substituted in β_1 as given above, we reach

$$\beta_1(\beta_2+3)^2(8\beta_2-9\beta_1-12) = (4\beta_2-3\beta_1)(10\beta_2-12\beta_1-18)^2$$

the equation to the biquadratic, proving that the point associated with the above frequency curve lies on the biquadratic.

Again $1-m$ will always be positive, or m less than unity. For the upper branch of the loop of the biquadratic lies below its asymptote, or $8\beta_2-9\beta_1-12\frac{2}{3} = 0$, and accordingly below the line $8\beta_2-9\beta_1-12 = 0$; thus the numerator of $1-m$ is always positive. So also is the denominator, for the upper branch always lies above the line $2\beta_2-3\beta_1-6 = 0$.[*]

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[*] In fact the R-line $(5\beta_2-6\beta_1-9=0)$ the parallel to the asymptote $(8\beta_2-9\beta_1-12=0)$, the limiting frequency line $(\beta_2-\beta_1-1=0)$, and the Type III. line $(2\beta_2-3\beta-6=0)$ meet in the point $\beta_2=-3$, $\beta_1=-4$ of the negative quadrant and the upper branch of the loop lies in the angle between the first two and in the positive quadrant.

As m is positive and less than unity the area and moments of the curve are all real and finite. When the point (β_2, β_1) moves along the loop of the biquadratic towards the R-point $(\beta_2 = 1\cdot8,\ \beta_1 = 0)$, the value of $1-m$ becomes more and more nearly unity, and ultimately at R we have $m = 0$, or the frequency curve is

$$y = y_0$$

a rectangle, *i.e.*, we reach the rectangle point. If on the other hand we move towards infinity along the upper branch of the biquadratic loop, we find $1-m$ approaches the value $1/\beta_1$ and thus ultimately becomes zero, or $m = 1$. Thus the limiting form of the frequency curve is a rectangular hyperbola, or rather the part of such hyperbola

$$y = y_0/(1+x/a)$$

from the vertical asymptote $x = -a$ to $x = 0$.

But this is clearly only a theoretical limit, for it involves $\beta_1 = \beta_2 = \infty$, and this means that if μ_2 be finite, μ_3 and μ_4 are infinite—results impossible in any actual frequency if the population be finite. It is clear indeed that β_2 must be less than N, for obviously $N\mu_4 < N^2\mu_2^2$. Again, β_1 is $< \beta_2 - 1$, and accordingly $\beta_1 < N-1$.[*] But these limits are of small service for practical statistics, where even for small samples, say, $N = 20$, they would scarcely ever be approached.[†] Thus the rectangular hyperbola can only be treated as a limiting form of Type VIII. far beyond the region of actual statistical experience.[‡] For practical purposes the point is that m is limited to values between 0 and 1, or Type VIII. ranges from the rectangle to the rectangular hyperbola. The suggestiveness of this is that curves in the I_U and the I_J areas, *i.e.*, above and below the upper branch of the biquadratic loop, must approach these types as they approach the extremes of this branch. Generally a U-curve near the biquadratic will be close to a curve resembling a curtailed hyperbola.

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[*] Mr. G. N. WATSON has given me a nearer limit to β_2, namely, $\beta_2 \leqq N - 2 + \dfrac{1}{N-1}$. But, except as showing that β_2 must be finite, which is otherwise obvious, this is again of no real service.

[†] The highest *observed* values that I know of for β_2 and β_1 are those given by DUNCKER ('Biometrika,' vol. VIII., p. 238). He gives

'Armzahl,' *Asterina exigua* $N = 600$ $\beta_2 = 33\cdot13$, $\beta_1 = 1\cdot76$,
,, *Archaster typicus* $N = 902$ $\beta_2 = 128\cdot48$, $\beta_1 = 4\cdot76$.

There are only three groups of frequency in each, 4, 5 and 6, and the bulk of the observations are concentrated in 5. The observations do not give, as he suggests, PEARSON'S Type IV. and Type VI. curves respectively; the κ_2 in *both* cases is less than unity, corresponding to Type IV. But both fall into the heterotypic area of Type IV. The attempt to fit with heterotypic curves would hardly be profitable until there was absolute certainty that the group with 4 'Armzahl' was not the result of accident.

[‡] *Theoretically* very high values of β_1 and β_2 can easily be found, *i.e.*, for samples of *four*, when the population sampled has, say, a correlation of 0·98; here the frequency curve for the correlation coefficient gives $\beta_1 = 203\cdot325$ and $\beta_2 = 311\cdot731$, but it is the rapidly approaching zero of μ_2 which leads to these results.

In concluding our discussion of this curve we may note that, perhaps, the easiest way of tracing the biquadratic is to calculate β_1 and β_2 from

$$\beta_1 = \frac{4(2\gamma-1)^2(\gamma+1)}{3\gamma-1}, \quad \beta_2 = \frac{3(\gamma+1+\beta_1)}{3-\gamma} = \frac{3(\gamma+1)(16\gamma^2-13\gamma+3)}{(3\gamma-1)(3-\gamma)}$$

by giving a succession of values to γ.

For $\gamma = 0{\cdot}5$ to 3 we get the points on the lower branch of the loop; for $\gamma = 0{\cdot}5$ to $0{\cdot}3$ we obtain the points on the upper branch of the loop. It will be seen that this amounts to taking the origin at $\beta_2 = -3$, $\beta_1 = -4$, and rotating a line through this point round it to intersect the curve. The slope of this line to the β_1 axis is $3/(3-\gamma)$.

The cubic, it may be here noted, which gives the Type V. curve may be traced from

$$\beta_1 = 4(\gamma^2-1), \quad \beta_2 = \frac{3(\gamma+1+\beta_1)}{3-\gamma} = \frac{3(\gamma+1)(4\gamma-3)}{3-\gamma}.$$

Here γ must be given values from 1 to 3.

The Type III. line, which passes through the Gaussian point, also passes through $\beta_2 = -3$ and $\beta_1 = -4$, and the above means of getting at the points on the cubic corresponds to finding the points in which a straight line passing through $(-4, -3)$ and rotating from the position of the Type III. line cuts the cubic—its slope in any position being as before $3/(3-\gamma)$.

Actually if θ be the angle between the above line from $(-4, -3)$ to the cubic, *i.e.*, $\tan\theta = 3/(3-\gamma)$,

$$r = 12\,(\sec\theta - \operatorname{cosec}\theta),$$

but to use this polar equation has not been found a very ready manner of plotting the cubic.*

(5) *Frequency Curve. Type IX.*—

$$y = y_0\left(1+\frac{x}{a}\right)^m.$$

Range from $x = -a$ to $x = 0$; y is zero at one end of the range and equal to y_0 at the other.

The analysis proceeds precisely as in the case of the curve of Type VIII., except that m is now opposite in sign. We have

$$y_0 = \mathrm{N}\,(1+m)/a,$$

$$\bar{x}\,(=\text{distance of mean from point } x = -a) = a\,(m+1)/(m+2),$$

$$\sigma^2 = \mu_2 = a^2(m+1)/\{(m+3)(m+2)^2\},$$

$$\mu_3 = -2a^3m\,(m+1)/\{(m+4)(m+3)(m+2)^3\},$$

$$\mu_4 = 3a^4(m+1)(3m^2+5m+4)/\{(m+5)(m+4)(m+3)(m+2)^4\},$$

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* The parts of the cubic and the quartic lying in the other three quadrants have been plotted by Miss B. C. B. Cave. Geometrically the interrelations of the two curves, their asymptotic and other critical lines are of much interest, but until some interpretation can be put on imaginary values of the moment coefficients, these interrelations have no statistical bearing.

leading to

$$\beta_1 = \frac{4m^2(m+3)}{(m+1)(m+4)^2}, \qquad \beta_2 = \frac{3(m+3)(3m^2+5m+4)}{(m+1)(m+4)(m+5)}.$$

Thus

$$m^3(\beta_1-4)+3m^2(3\beta_1-4)+24m\beta_1+16\beta_1 = 0$$

would give m, and a would be found from

$$a = \pm\sigma(m+2)\sqrt{\frac{m+3}{m+1}}.$$

the sign being found from the observed value of μ_3. Lastly

$$y_0 = \frac{\text{N}}{\sigma}\frac{m+1}{m+2}\sqrt{\frac{m+1}{m+3}}.$$

Practically it is better to determine m from

$$m = \frac{2(5\beta_2-6\beta_1-9)}{3\beta_1-2\beta_2+6},$$

which value of m substituted in the expression for β_1 gives the biquadratic.

Clearly since the lower branch of the biquadratic lies below the line $5\beta_2-6\beta_1-9=0$, m is positive until the line $2\beta_2-3\beta_1-6=0$ is reached, and in this section of the branch, *i.e.*, from $m=0$ to $m=\infty$, or from $\beta_2 = 1\cdot8$, $\beta_1 = 0$ up to $\beta_2 = 9$, $\beta_1 = 4$ (the exponential point, E) occurs an interesting isolated point—the line-point L. When $\beta_2 = 2\cdot4$, $\beta_1 = 0\cdot32$, then $m = 1$, and Type IX. degenerates into a sloping straight line, $y = y_0(1+x/a)$, or the frequency *line* is

$$y = \frac{\sqrt{2}\text{N}}{3\sigma}\left(1+\frac{x}{3\sqrt{2}\sigma}\right).$$

Up to the line-point, Type IX. curve rises at $x=-a$ *perpendicular* to the axis of x, at the line-point it makes a finite angle less than 90 degrees, and after the line-point we start with contact at $x=-a$.

It is interesting to note the sloping line arising as a case of these generalised frequency curves, and we observe that its locus is separated from the rectangle locus by a considerable interval along the biquadratic in which the curve of Type IX. is very trapezoidal in form.

(6) *Frequency Curve of Type X. The Exponential Curve.*—Beyond the line-point, L at $\beta_2 = 2\cdot4$, $\beta_1 = 0\cdot32$, we reach as m steadily mounts a series of frequency curves which culminate in the exponential curve at E or $\beta_2 = 9$, $\beta_1 = 4$.

Clearly

$$y_0 = \text{N}\frac{m+1}{a} = \frac{\text{N}}{\sigma}\frac{m+1}{m+2}\sqrt{\frac{m+3}{m+1}} = \frac{\text{N}}{\sigma} \text{ when } m \text{ is infinite.}$$

Further

$$y = \frac{\mathrm{N}}{\sigma}\left(1 \pm \frac{x}{\sigma(m+2)}\right)^{(m+2)-2},$$

$$= \frac{\mathrm{N}}{\sigma} e^{\pm x/\sigma},$$

the range being from $x = 0$ to $-\infty$, if we take the positive sign—and from $x = 0$ to $+\infty$, if we take the negative. It is thus sufficient to consider

$$y = \frac{\mathrm{N}}{\sigma} e^{\pm x/\sigma},$$

with range from $x = 0$ to $x = +\infty$. The first two moments of the area about $x = 0$ are $\nu'_1 = \sigma$ and $\nu'_2 = \sigma^2$. Thus $\bar{x} = \sigma$ and $\mu_2 = \sigma^2$, as it should. Lastly, $\mu_3 = 2\sigma^3$ and $\mu_4 = 9\sigma^4$.

The fitting of the exponential curve presents no difficulty.

The exponential point E is a transition point of great interest as being even more than the Gaussian point G—the meeting point of many types. At E, Type IX. changes to Type XI., but at E the familiar Type III. passes from a zero ordinate at the limited end of the range to a J-curve with infinite ordinate. Further, E is a point at which the areas of Type I. (Type $\mathrm{I_L}$) as a limited range with zero ordinates at its terminals, and as a limited range with one infinite ordinate at a terminal (Type $\mathrm{I_J}$) meet. Finally, Type VI. area, which lies between Type III. line and Type V. cubic, is divided into two sections by Type XI., which lies along the lower branch of the biquadratic loop below E. Below the biquadratic, Type VI. takes the form

$$y = y_0 (x-a)^{q_2}/x^{q_1},$$

with a range from $x = a$ to ∞, q_1 and q_2 being both positive. In the area, however, below Type $\mathrm{III_J}$ and above Type XI., Type VI. takes the form $\mathrm{VI_J}$, or the J-shaped curve

$$y = \frac{y_0}{x^{q_1}(x-a)^{q_2}},$$

with a range from $x = a$ to $x = \infty$. In this case $r = 6(\beta_2 - \beta_1 - 1)/(3\beta_1 - 2\beta_2 + 6)$ will be negative, since we are below the line $2\beta_1 - 3\beta_1 - 6 = 0$. Further, ϵ is negative since we are above the cubic or Type V. branch

$$4(4\beta_2 - 3\beta_1)(2\beta_2 - 3\beta_1 - 6) = \beta_1(\beta_2 + 3)^2.$$

Thus our quadratic

$$m'^2 - rm' + \epsilon = 0,$$

corresponds of necessity to real roots, of which one will be negative and the other positive. The positive root will be

$$\tfrac{1}{2}\left(\sqrt{r^2 - 4\epsilon} + r\right),$$

and is therefore numerically the smaller root since r is negative; it will be less than unity, and therefore $m'-1 = m$ will be negative if

$$\tfrac{1}{2}(\sqrt{r^2-4\epsilon}+r)<1,$$

or

$$\epsilon-r+1>0,$$

but this is the condition for the point β_1, β_2 lying inside the loop of the quadratic. Thus in this case we reach the J-shaped curve of Type VII., or

$$y = \frac{y_0}{x^{q_1}(x-a)^{q_2}}.$$

In order that the area of this curve and its moments should be finite, it is clearly needful that q_2 should be less than unity.

(7) *Frequency Curve. Type XI.*—Beyond the exponential point the lower branch of the biquadratic is below the line $2\beta_2-3\beta_1-6 = 0$, and consequently m is again negative and the curve takes the form

$$y = y_0 x^{-m},$$

where

$$m = \frac{2(5\beta_2-6\beta_1-9)}{2\beta_2-3\beta_1-6}.$$

The range is, however, only limited in one direction, it is from $x = b$ to $x = \infty$, say.

This lower branch of the biquadratic loop tends to become vertical and asymptotic to the line $\beta_1 = 50$. Hence m takes all values from ∞ down to 5.

Clearly, for moments about $x = b$,

$$\mathrm{N}\mu'_p = \frac{y_0}{m-p-1}\,\frac{1}{b^{m-p-1}},$$

and these will be real and finite if $p < m-1$, or only the fourth moment would fail at the limit $\beta_2 = \infty$, which indeed cannot in practice be reached. At the same time if we want the probable error of the fourth moment to be finite, it is needful that μ'_8 should be finite or we must have $m > 9$. Thus $m = 9$ must be where the curve passes into the heterotypic region and becomes of doubtful application.

We easily find from the above result for μ'_p

$$\bar{x} = b(m-1)/(m-2), \qquad \mu_2 = \sigma^2 = b^2(m-1)/\{(m-2)^2(m-3)\},$$

$$\mu_3 = 2b^3 m(m-1)/\{(m-2)^3(m-3)(m-4)\},$$

$$\mu_4 = 3b^4(m-1)(3m^2-5m+4)/\{(m-2)^4(m-3)(m-4)(m-5)\},$$

leading to

$$\beta_1 = \frac{4m^2(m-3)}{(m-1)(m-4)^2}. \qquad \beta_2 = \frac{3(m-3)(3m^2-5m+4)}{(m-1)(m-4)(m-5)}.$$

Thus for $m = 9$ we find $\beta_1 = 9{\cdot}72$, $\beta_2 = 22{\cdot}725$, which satisfy the equation $8\beta_2-15\beta_1-36 = 0$ of the heterotypic line.

m may be found from

$$m = \frac{2\,(5\beta_2-6\beta_1-9)}{2\beta_2-3\beta_1-6},$$

or from β_1 alone by the cubic

$$m^3\,(4-\beta_1)+m^2\,(9\beta_1-12)-24\beta_1 m+16\beta_1 = 0,$$

then

$$b = \pm\sigma\,(m-2)\sqrt{\frac{m-3}{m-1}},$$

and

$$y_0 = \mathrm{N} b^{m-1}\,(m-1),$$

while the mean $\bar{x} = b\,(m-1)/(m-2)$ enables us to place the curve on the observations.

There is no discontinuity in the form of the curve down to $m = 5$, but only discontinuity after $m = 9$ in the probable errors of its moment-coefficients.

The curve starts with a finite ordinate and meets that ordinate at a finite angle; it asymptotes to the x-axis at $x = \infty$, and has no point of inflexion except at infinity.

(8) *Frequency Curve. Type XII.*—

$$y = y_0\left(\frac{\sigma\,(\sqrt{3+\beta_1}+\sqrt{\beta_1})+x}{\sigma\,(\sqrt{3+\beta_1}-\sqrt{\beta_1})-x}\right)^{\sqrt{\frac{\beta_1}{3+\beta_1}}}.$$

This J-curve arises along the R-line, or $5\beta_2-6\beta_1-9 = 0$. Its range is from $x = \sigma\,(\sqrt{3+\beta_1}-\sqrt{\beta_1})$ to $x = -\sigma\,(\sqrt{3+\beta_1}+\sqrt{\beta_1})$, and then its mean is the origin. When β_1 is zero it degenerates into a rectangle (*i.e.*, at the rectangle point).

In order to illustrate the nature of the curve more fully let us start from the general equation which arises when the denominator of the differential equation has real roots,[*] *i.e.*,

$$y = y_0\,(1+x/a_1)^{m_1}\,(1-x/a_2)^{m_2},$$

where

$$y_0 = \frac{\mathrm{N}}{b}\,\frac{m_1^{\,m_1}m_2^{\,m_2}}{(m_1+m_2)^{m_1+m_2}}\,\frac{\Gamma\,(m_1+m_2+2)}{\Gamma\,(m_1+1)\,\Gamma\,(m_2+1)}$$

and

$$\frac{m_1}{a_1} = \frac{m_2}{a_2} = \frac{m_1+m_2}{b},$$

the origin being the mode and b the range.

Transferring to the mean as origin[†] this becomes

$$y = \frac{y_0}{a_1^{\,m_1}a_2^{\,m_2}}\left(\frac{b\,(m_1+1)}{m_1+m_2+2}+x\right)^{m_1}\left(\frac{b\,(m_2+1)}{m_1+m_2+2}-x\right)^{m_2},$$

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[*] 'Phil. Trans.,' A, vol. 186, p. 369.

[†] *Loc. cit.*, p. 370.

where*

$$b = \tfrac{1}{2}\sigma \left\{\beta_1 (m_1+m_2+4)^2 + 16 (m_1+m_2+3)\right\}^{1/2}.$$

$$\frac{y_0}{a_1^{m_1}a_2^{m_2}} = \frac{\mathrm{N}}{b^{m_1+m_2+1}} \frac{\Gamma(m_1+m_2+2)}{\Gamma(m_1+1)\,\Gamma(m_2+1)},$$

on substitution for a_1 and a_2 as above.

Now put $m_1+m_2 = 0$, or $m_2 = -m_1 = m$, say.

Then

$$y = \frac{\mathrm{N}\,.\,\Gamma(2)}{b\Gamma(1+m)\,\Gamma(1-m)} \left(\frac{b(m+1)}{2}+x\right)^m \left(\frac{b(1-m)}{2}-x\right)^{-m},$$

while

$$b = \tfrac{1}{2}\sigma \left\{16\beta_1+48\right\}^{1/2} = 2\sigma (\beta_1+3)^{1/2}.$$

It remains to find m.

Now m_1 and m_2 are the roots of†

$$m^2-(r-2)\,m+\epsilon-r+1 = 0,$$

where

$$r = \frac{6(\beta_2-\beta_1-1)}{3\beta_1-2\beta_2+6} = m_1+m_2+2,$$

$$\epsilon = \frac{(m_1+m_2+2)^2}{4+\frac{1}{4}\beta_1(m_1+m_2+4)^2/(m_1+m_2+3)}$$

Hence, when $m_1+m_2 = 0$, we have

$$r = 2 \quad \text{or} \quad 5\beta_2-6\beta_1-9 = 0, \text{ the R-line,}$$

and

$$\epsilon = 3/(\beta_1+3).$$

Whence

$$m^2 = 1-\epsilon \quad \text{or} \quad m = \pm\sqrt{\frac{\beta_1}{3+\beta_1}}.$$

But $\Gamma(2) = 1$, and it is well known that

$$\Gamma(1+m)\,\Gamma(1-m) = \frac{m\pi}{\sin m\pi}.$$

Thus

$$y = \frac{\mathrm{N}}{2\pi\sigma} \frac{\sin\left\{\sqrt{\frac{\beta_1}{3+\beta_1}}\,\pi\right\}}{\sqrt{\beta_1}} \left(\frac{\sigma(\sqrt{3+\beta_1}+\sqrt{\beta_1})+x}{\sigma(\sqrt{3+\beta_1}-\sqrt{\beta_1})-x}\right)^{\sqrt{\frac{\beta_1}{3+\beta_1}}}.$$

This is the full equation to the R-line J-curve, the mean being origin.‡ It requires for its determination only a knowledge of β_1, but we must be also certain that the

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* *Loc. cit.*, p. 369.

† *Loc. cit.*, pp. 368–9. Deduced at once from $m'^2-rm'+\epsilon = 0$ by putting $m' = m+1$.

‡ The sign of $\sqrt{\beta_1}$ in $\sigma(\sqrt{3+\beta_1} \pm \sqrt{\beta_1})$ must be determined from that of μ_3.

condition $5\beta_2-6\beta_1-9=0$ is satisfied within the limits of random sampling. Its possibilities extend from $\beta_1=0$ to $\beta_1=\infty$. When $\beta_1=0$,

$$y=\frac{\mathrm{N}}{2\sqrt{3}\sigma},\text{ the rectangle.}$$

Now consider what happens for any frequency curve of the limiting character when *both* β_1 and β_2 become infinite, say, in the ratio $\beta_2=p\beta_1$. Then

$$r=\frac{6(p-1)}{3-2p},$$

and accordingly r will be finite if p is finite, except along the Type III. line. Accordingly for $\beta_1=\infty$, ϵ will be zero. Thus the ratio of β_2 to β_1 is from their values,

$$\beta_2/\beta_1=\tfrac{3}{2}\cdot\frac{r+2}{r+3}=p,$$

which agrees with the above result for r.

For the special case when $r=2$, we have $p=\tfrac{6}{5}$, which agrees with the limiting ratio of β_2/β_1 along the R-line.

Now when $\epsilon=0$ we have from

$$m^2-(r-2)m+\epsilon-r+1=0,$$

$$m=\tfrac{1}{2}\left(r-2\pm\sqrt{(r-2)^2+4r-4}\right),$$

$$=\tfrac{1}{2}(r-2\pm r)=r-1\text{ or }-1.$$

Thus from the equations on page 445,

$$y=\frac{\mathrm{N}}{b}\frac{\Gamma(m_1+m_2+2)}{\Gamma(m_1+1)\Gamma(m_2+1)}\left(\frac{m_1+1}{m_1+m_2+2}+\frac{x}{b}\right)^{m_1}\left(\frac{m_2+1}{m_1+m_2+2}-\frac{x}{b}\right)^{m_2},$$

$$=\frac{\mathrm{N}(m_2+1)}{b}\frac{1}{\Gamma(m_2+2)}\left(\frac{r}{r}+\frac{x}{b}\right)^{r-1}\left(-\frac{x}{b}\right)^{-1},$$

$$=\frac{\mathrm{N}(m_2+1)}{x}\left(1-\frac{x}{b}\right)^{r-1},$$

if we change the sense of the axis of x and take x from 0 to $+b$.

Now in order that σ should be finite it is needful that b should be infinite when $m_2=-1$, for

$$\sigma^2=b^2(m_2+1)/\{r(r+1)\}.$$

But if b be infinite, $y=0$ owing to the factor m_2+1, for every value of x, except $x=0$. Hence the frequency is a concentrated lump at $x=0$, and this involves of itself $\sigma=0$.

But if $\sigma = 0$, b must be finite or zero, and these both again throw us back on a concentrated frequency at $x = 0$.

Accordingly, when β_1 and β_2 both become infinite, we deal with a concentrated frequency lump. But the ratio of β_1 to β_2 will depend on the manner in which we have reached this limiting case.

For example, if we are dealing with the correlations in samples of two drawn from a population in which the correlation is ρ, the frequency consists of two lumps, but as ρ approaches unity, one lump shrivels up, β_1 and β_2 both become infinite, but their ratio is one of equality, *i.e.*, we approach infinity along the line $\beta_2 - \beta_1 - 1 = 0$.

When we take samples of three from a population of correlation ρ, the frequency curves are U-shaped, but as ρ approaches unity the frequency concentrates in one leg of the U, β_1 and β_2 both become indefinitely larger, but their ultimate ratio β_2/β_1 appears to equal $\frac{5}{4}$.* The U-curve flattens down into an L-curve, of which the horizontal limb extends to infinity and becomes indefinitely thin, while the vertical limb contains all the frequency.

(9) *Scheme of Skew Frequency Curves Represented as a Diagram.*—We are now able to considerably enlarge our diagrammatic representation of frequency curves. (See Diagram, Plate 1.)

Every distribution is represented by its characteristic co-ordinates β_1 and β_2, which must be positive, and therefore we need only deal with the positive β_1, β_2 quadrant. No frequency distribution at all can lie above the line $\beta_2 - \beta_1 - 1 = 0$; this restriction removes more than half the positive quadrant. No frequency distribution can be adequately represented by one of the present system of skew curves, if it falls below the line $8\beta_2 - 15\beta_1 - 36 = 0$. The area below this line is therefore termed *heterotypic*. Heterotypic distributions are to say the least of it very rare, if they be not extremely improbable. We have seen that there is some reason to suppose that bimodal distributions would give rise to such heterotypic distributions, but with our present views as to frequency such distributions when they do not arise from the mere anomalies of random sampling are classed as heterogeneous, and supposed to be due to mixtures.

Having thus limited our area at top and bottom we proceed to consider the various possibilities that arise.

The β_2-axis, where $\beta_1 = 0$, is the axis of *symmetrical* frequency distributions. Possibilities begin at the B-line or the point $\beta_2 = 1$, or we have two equal concentrated frequency blocks at any arbitrary distance b. This is the case of two alternative values, either of which is equally probable. For example, heads or tails in the repeated tossings of a single coin, or positive or negative perfect correlation in samples of two taken from a population of individuals bearing two uncorrelated

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* I use the word "appears" advisedly, because the ratio has been obtained by determining the value of β_2/β_1 for high numerical value of ρ. The actual ratio for $\rho = 1$ depends upon approaching a limit in rather complicated elliptic integral expressions, which I have not yet accomplished.

characters. Below the point $\beta_2 = 1$, descending the β_2-axis, the two concentrated frequencies expand into a symmetrical U-curve. This is Type II_{U} with the equation

$$y = y_0\,(1-x^2/a^2)^{-m}$$

and the criterion $\beta_1 = 0$, $\beta_2 < 1{\cdot}8$.

Here*

$$m = \tfrac{1}{2}\,(9-5\beta_2)/(3-\beta_2),$$

$$a^2 = \sigma^2\,.\,2\beta_2/(3-\beta_2),$$

and

$$y_0 = \frac{\mathrm{N}}{\sqrt{2\pi}\sigma}\,\frac{\Gamma\,(\frac{3}{2}-m)}{\Gamma\,(1-m)\,\sqrt{\frac{3}{2}-m}}.$$

When $\beta_2 = 1{\cdot}8$, $m = 0$, and we reach the "rectangle-point" R. Here $y_0 = \mathrm{N}/(2a)$ and $\sigma = a/\sqrt{3}$.

Samples of three individuals from a population whose individuals carry two uncorrelated characters give a symmetrical U-frequency for the coefficients of correlation of those characters in triplets of individuals. In this illustration $\beta_2 = 1{\cdot}5$. Samples of four individuals from the same population give a rectangle for the frequency distribution of the coefficients of correlation. Passing still lower down the axis of symmetrical frequency the type is now Type II_{L}, or the limited range frequency curve

$$y = y_0\,(1-x^2/a^2)^{m}$$

and the criterion is $\beta_1 = 0$, $\beta_2 > 1{\cdot}8 < 3$.

In this range m increases from 0 to ∞, and

$$m = \tfrac{1}{2}\,(5\,\beta_2-9)/(3-\beta_2)$$

$$a^2 = \sigma^2\,.\,2\,\beta_2/(3-\beta_2),$$

$$y_0 = \frac{\mathrm{N}}{\sqrt{2\pi}\sigma}\,\frac{\Gamma\,(\frac{3}{2}+m)}{\Gamma\,(1+m)\,\sqrt{\frac{3}{2}+m}}.$$

We see that the range grows greater as m approaches infinity, or $\beta_2 = 3$, when we reach G the Gaussian point ($\beta_1 = 0$, $\beta_2 = 3$).

If samples of n individuals be taken from an indefinitely large population in which the individuals carry two uncorrelated characters, then if n be 5 or over, all the frequency curves of the correlation coefficients of these samples are of Type II_{L}, only approaching the Gaussian when n is very considerable indeed. For example when $n = 25$, $\beta_2 = 2{\cdot}7692$, and the frequency is still a good way from the Gaussian. When $n = 400$, $\beta_2 = 2{\cdot}9850$, it is thus fairly close to it, but is not coincident.

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* It is, perhaps, worth noticing that for $\beta_2 = 15/7$ we obtain the ordinary parabola as a special type of frequency-curve.

After we have passed the Gaussian point we obtain curves of unlimited range of Type VII., of which the equation is

$$y = y_0 (1+x^2/a^2)^{-m},$$

The range of β_2 is from 3 to ∞ and

$$m = \tfrac{1}{2}(5\beta_2-9)/(\beta_2-3),$$

falls from infinity to 2·5; while

$$a^2 = \sigma^2 . 2\beta_2/(\beta_2-3),$$

$$y_0 = \frac{\text{N}}{\sqrt{2\pi}\sigma} \frac{\Gamma(m)}{\Gamma(m-\frac{1}{2})\sqrt{(m-\frac{3}{2})}}.$$

Illustration of curves of Type VII.* are not infrequent in biological statistics. We see that the Gaussian is a mere point in an infinite range of symmetrical frequency curves, and a single point in a doubly infinite series of general frequency distributions.

Now let us consider the asymmetrical frequency curves displayed on the Diagram. If we approach from the "impossible area" we reach on the B-line the first available type of frequency—the alternative concentrated blocks. At one end of the B-line we have two equal isolated frequencies, and at the other a single isolated frequency.

Crossing the B-line we reach the area of limited range U-shaped curves, *i.e.*, Type I_U, which has for its equation :

$$y = y_0 (1+x/a_1)^{-m_1} (1-x/a_2)^{-m_2}.$$

This U-area extends as far as the upper branch of the loop of the biquadratic, the asymptote of which, $24\beta_2-27\beta_1-38 = 0$, is indicated by a broken line. In U-shaped frequency curves both m_1 and m_2 are necessarily less than unity, for their product is $\epsilon-r+1$, which is less than unity and positive above the upper branch of the biquadratic (*i.e.*, $\epsilon-r+1 = 0$). Type I_U is fitted as Type I. (see 'Phil. Trans.,' A, vol. 186, p. 367), and has been illustrated by me ('Roy. Soc. Proc.,' vol. 62, p. 287), by fitting curves of frequency to cloudiness. The frequency curves for the correlation coefficients of samples of three drawn from a population whose individuals have two characters of any degree of correlation are also skew U-shaped frequency curves, although their algebraic form has not the above simplicity.

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* Type II_L was discussed in my first memoir, 'Phil. Trans.,' vol. 186, p. 372. Type II_J and Type VII. are briefly referred to in 'Biometrika,' vol. IV., p. 174, but, unfortunately, with some rather disturbing misprints. They are correctly placed on RHIND's diagram, 'Biometrika,' vol. VII., p. 131, but the formulæ for fitting are not given. The formulæ have been given for many years in lecture-notes, and the curves have been frequently used.

On the upper branch of the biquadratic loop we reach curves of Type VIII., *i.e.*,

$$y = y_0 \, (1+x/a)^{-m},$$

discussed on p. 444 of the present memoir. Here m is less than unity.

We now pass into the loop of the biquadratic between the upper branch and the R-line. Here we have J-curves, Type I_{J}, of the form

$$y = y_0 \, (1+x/a_1)^{-m_1} \, (1+x/a_2)^{-m_2}$$

where m_2 is less than unity, and m_1 is less than m_2.

Coming to the R-line, m_1 becomes equal to m_2 and we have Type XII., or

$$y = y_0 \left(\frac{\sigma\left(\sqrt{3+\beta_1}+\sqrt{\beta_1}\right)+x}{\sigma\left(\sqrt{3+\beta}-\sqrt{\beta_1}\right)-x}\right)^{\sqrt{\frac{\beta_1}{3+\beta_1}}}$$

discussed on p. 446 of the present memoir. Below the R-line, we return to Type I_{J}, but m_1 is now greater than m_2.*

We now reach the lower branch of the biquadratic loop. This is divided into three portions by three critical points. The first portion is from the rectangle-point (R) to the line-point L. In this portion we start from R with the curve of Type IX. or,

$$y = y_0 \, (1+x/a)^m$$

for $m = 0$, or the rectangle, and proceed from that value to $m = 1$, which gives us the line (or triangle); the range is $-a$ to 0. Since m is always < 1, the curve rises perpendicularly at $x = -a$, and approximates to a trapezoidal form. The method of fitting is discussed in this memoir, p. 441. The fitting of the line curve

$$y = y_0 \, (1+x/a)$$

is dealt with on p. 442.

Beyond the line-point L we have Type IX_2 which differs in no way from Type IX_1, except that m is now greater than unity, and there is contact of a rapidly increasing order at $x = -a$.

When $m = \infty$ we find Type X. the exponential curve, at the exponential point E. The fitting of this curve

$$y = \frac{\mathrm{N}}{\sigma} e^{-x/\sigma}$$

has been discussed on p. 443.

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* For example, at the point $\beta_2 = 4$, $\beta_1 = 2$, between the R-line and upper branch,

$$y = y_0 \left(1 + \frac{x}{a_1}\right)^{0{\cdot}2123} \Big/ \left(1 + \frac{x}{a_2}\right)^{0{\cdot}7123},$$

but at $\beta_2 = 8$, $\beta_1 = 4$, between the R-line and the lower branch,

$$y = y_0 \left(1 + \frac{x}{a_1}\right)^{7{\cdot}4011} \Big/ \left(1 + \frac{x}{a_2}\right)^{0{\cdot}4011}.$$

Since E is the junction of several types, we turn to consider Type III. which is the curve found along the critical line

$$2\beta_2 - 3\beta_1 - 6 = 0.$$

It passes through the Gaussian point G, and its equation is

$$y = y_0 \, (1 + x/a)^p \, e^{-px/a}.$$

It is fully discussed in my first memoir; see 'Phil. Trans.,' A, vol. 186, p. 373, *et seq.*

From G to the exponential point E, p ranges from ∞ to zero, which latter value provides the exponential curve. After the exponential point p becomes negative and we reach Type III_J, a J-curve with range limited in one direction only. This curve separates the doubly limited curves of Type I_J from curves of Type VI_J, which lie below the line $2\beta_2 - 3\beta_1 - 6 = 0$, and above the lower branch of the biquadratic loop. On this lower branch of the loop we have Type XI., or the form

$$y = y_0 x^{-m}$$

the range being from an arbitrary value b to ∞, and m ranging from ∞ to 5. This type is fully discussed in the present memoir; see p. 444. It continues right away along this branch of the biquadratic, but at $\beta_2 = 22{\cdot}725$ and $\beta_1 = 9{\cdot}72$, the eighth moment of the theoretical curve would become infinite, and accordingly the probable error of the fourth moment coefficient would become *theoretically* infinite. Thus since the fitting of the curve depends on the fourth moment its constants would cease to be reliable measures of the distribution. We enter at this point the "heterotypic area," for this type of curve.* We have now two further areas to clear off, namely those between the Type III. line and the lower branch of the biquadratic loop. Above the former and below the latter we have the range of double limited frequency curves, *i.e.*, Type I_L, or

$$y = y_0 \, (1 + x/a_1)^{m_1} \, (1 - x/a_2)^{m_2}.$$

This curve was fully discussed in my first memoir ('Phil. Trans.,' A, vol. 186, p. 376, *et seq.*) m_1 and m_2 are both positive, and experience has shown that probably the bulk of all frequency distributions cluster into this area.

Above the biquadratic loop and below the line $2\beta_2 - 3\beta_1 - 6 = 0$, we have curves of Type VI_J, or

$$y = \frac{y_0}{x^{q_1} \, (x - a)^{q_2}}$$

with range from $x = a$ to $x = \infty$.

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* Of course, by using the actual eighth moment of the data, instead of the eighth moment of the theoretical curve, the standard deviation of the fourth moment would be finite, but this procedure would really indicate that, as far as the high moments are concerned, curve and data were discordant, and that we should not really be finding the probable error of a constant of our theoretical frequency curve.

They have been considered on p. 443 of the present memoir. Their full theory is precisely that of curves of Type VI. in general, discussed in the first supplement to my memoir on skew variation ('Phil. Trans.,' A, vol. 197, p. 448, *et seq.*). The only point to be emphasised is that the q_2 of Equation XIX. of that memoir in this area is negative and less than unity. The treatment is identical.

Below both the Type III. line and the biquadratic, we have a space bounded by the cubic

$$4(4\beta_2-3\beta_1)(2\beta_2-3\beta_1-6) = \beta_1(\beta_2+3)^2.$$

This is the area of Type VI. proper, *i.e.*,

$$y = y_0(x-a)^{q_2}/x^{q_1}$$

with range from $x = a$ to $x = \infty$, $q_2 < q_1$ being positive, and is fully discussed in the memoir just cited.

The area of Type VI. is limited by the above cubic along which Type V., or,

$$y = y_0 x^{-p} e^{-\gamma/x}$$

from $x = 0$ to $x = \infty$, describes the frequency. Its full consideration will be found in 'Phil. Trans.,' A, vol. 197, p. 446, *et seq.* Below the Type V. cubic we reach the area of Type IV. curve, or

$$y = y_0 e^{-\nu \tan^{-1}(x/a)}/(1+(x/a)^2)^m.$$

This has unlimited range in both directions and its treatment is fully discussed in my first memoir ('Phil. Trans.,' A, vol. 186, p. 376, *et seq.*). Theoretically, Types IV. and VI. describe all types lying below the line $2\beta_2-3\beta_1-6 = 0$. The objection to their use lies in the increasing probable errors of their constants, however good their general fit may be. To warn the statisticians of this, the line $8\beta_2-15\beta_1-36 = 0$, is drawn on the diagram and the area below it is marked "heterotypic area." I use this term to signify that it is doubtful whether my skew-frequency curves, depending only on the first *four* moments, can adequately describe distributions of types falling below this line; they require the use of the fifth and higher moment coefficients. Their occurrence in practice, however, must be rare.

It will be noticed that the line $\beta_2-\beta_1-3 = 0$ is drawn through the Gaussian point. This is the relation which must be satisfied in the case of POISSON's exponential limit to the binomial. Hence, in the case of a distribution with β_1, β_2, near this line, it is worth while investigating whether the "law of small numbers" is appropriate. Above this line every real binomial distribution, *i.e.*, cases of p and q both positive and less than unity, and n positive (taking the binomial as $(p+q)^n$) must lie, for

$$\frac{\beta_2-3}{\beta_1} = \frac{1-6pq}{1-4pq},$$

and the right-hand side is clearly less than unity. This limited area covered by the real binomial explains its relative infrequency as a descriptive series in practical statistics. If, however, we take the negative binomial as admissible, *i.e.*, allow forms of the type

$$(p-q)^{-n}, \quad \text{where} \quad p-q = 1$$

we extend the possible area of a binomial down to the line $2\beta_2 - 3\beta_1 - 6 = 0$.

Such a type of binomial is by no means of infrequent occurrence and can be more or less justified on *a priori* grounds.* Below Type III. line, the values of p and q become in the mathematical sense unreal, *i.e.*, imaginary. It is by no means certain, however, that such imaginary binomials with real moment coefficients may not, like imaginary hypergeometricals, give statistically good fits and be ultimately provided with physical interpretations.

(10) *Concluding Remarks.*—It is very difficult to assert finality for any scientific investigation, but I trust this second supplement to my original memoir on skew variation of 1894 has garnered the last harvest of possible types within the limits proposed in that investigation. The object was the discovery of a system of frequency curves providing for every possible variation of the first four moment coefficients of a distribution and provision for their rapid treatment and calculation. Since 1894 much has been done by the provision of tables of the new functions and improved tables of old functions necessary to carry this out.† Diagrams like that accompanying this memoir, enable the statistician who has calculated the characteristic β_1 and β_2, to select at once the appropriate type, from the position of the point β_1, β_2 in the β_1, β_2 plane. The first diagram, prepared by Mr. A. J. RHIND at my suggestion, has been long in use.‡ For the present very carefully prepared and much extended diagram I have to thank my colleague, Miss ADELAIDE G. DAVIN, whose labours cannot fail to be appreciated by those having to handle practically statistical data.

Since the publication of my original memoir on skew variation, many attempts have been made to express the nature of skew distributions by other systems of curves or by expansions in series. I have given careful attention to these competing systems and have discussed some of them elsewhere ('Biometrika,' vol. IV., pp. 169 to 212). My chief objections to them arise from the fact that they either (i.) cover far less than the necessary area; or (ii.) involve constants the probable errors of which can be indefinitely great; or (iii.) involve constants the probable errors of which have not been or possibly cannot be calculated. In no case that I know of have they systematically been applied to extensive ranges of data, and the goodness of fit compared with that of other systems. The existence of such competing systems is at any rate

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* See 'Biometrika,' vol. IV., p. 209, and vol. XI., p. 139.

† Now collected in "Tables for Statisticians and Biometricians," issued by the Cambridge University Press.

‡ 'Biometrika,' vol. VII., p. 131.

noteworthy evidence that to attempt to describe frequency by the Gaussian curve is hopelessly inadequate. It is strange how long it takes to uproot a prejudice of that character! If the reader will turn again to the present diagram, he will see that the Gaussian frequency occupies a *single point* in an indefinitely extended area. Those who support the Gaussian theory have to prove that no distribution occurs at a distance from the point G of our diagram greater than could be accounted for by the probable errors of sampling of β_1 and β_2. These errors are known and have been tabled[*] and that position is quite untenable. Frequency distributions occur every day which by no manner of means can be described by Gaussian systems.

It has been said that my skew curves suddenly change their algebraic type and that the statistician is puzzled by a slight change in the constants β_1 and β_2 involving such radical changes in the equation to the type. But if the reader examines the present diagram, he will see that the main Types I_U, I_J, I_L, IV., VI. and VI_J occur in *areas*, while the remaining types occur in the critical curved or straight lines which bound these areas. Special cases like the Gaussian, the exponential or the rectangular distributions occur where critical lines intersect. Now all these critical lines are really critical in the sense that a change of important physical significance occurs in this neighbourhood, and it is very unlikely that physical changes will be unaccompanied by sharp algebraical changes of form, such as are directly obvious in my curves, but are disguised by discontinuities in some of the proposed alternative expressions in series.[†]

Any *one* illustration that the frequencies which occur in actual statistical data can practically cover the whole possible area of the β_1, β_2 planes, and can present frequency distributions which change abruptly in type, will suffice to confute both the argument that frequency is concentrated in or near the Gaussian point, and the argument that it is undesirable that skew-frequency curves should be so manifold in form, although how they are to change from U to J, to "cocked hat," to rectangle and to exponential forms without this abrupt change will be a puzzling problem to solve for the professed mathematician. An illustration of this character has been several times referred to in the course of this paper. Let us suppose there exists an indefinitely large population, each individual of which carries any number of characteristics which are correlated together, for simplicity we will say according to the normal law. We may suppose that there are enough pairs of characters to give all values of the correlation ρ from $+1$ to -1.

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[*] 'Tables for Statisticians and Biometricians,' pp. 68–71.

[†] An analogy might be given in the case of the expression of a "cocked-hat" shape of finite range and a U-shaped distribution by a *single* FOURIER'S series. Here the trigonometrical expression by the FOURIER'S series would be superficially the same if kept in symbolic form, while the algebraic form of the U-curve would require two vertical asymptotes and its equation would be wholly different from that of the "cocked-hat' form. The Fourier expression would only disguise the real discontinuity. In the same manner real discontinuity of form is disguised in the series which express skew frequency in terms of a long series of moment coefficients.

Now from this population we will take a large number m of samples of n individuals. If in each one of these samples we calculate the correlation, r, between two variates, then r will not be equal to the value of ρ in the sampled population, but the m samples will give a frequency curve for r, which is limited in range between $+1$ and -1 and is determined by n the number of individuals in the sample and by ρ the correlation of the characters in the indefinitely large population sampled. We thus obtain a doubly infinite series of frequency distributions. The general theory of such distributions has been worked out by "STUDENT" ('Biometrika' vol. VI., p. 302, *et seq.*), Mr. H. E. SOPER (*Ibid.*, vol. IX., p. 91, *et seq.*), and Mr. R. A. FISHER (*Ibid.*, vol. X., p. 507, *et seq.*). The actual forms of the frequency curves are not usually expressible by simple single functions, but the ordinates and the β_1, β_2 admit of numerical determination. The calculations are extremely laborious, but up to the present the members of my laboratory staff have calculated some 270 frequency curves with nearly 40 ordinates each for values of ρ ranging from 0 to 1, and of n from 2 to 400. The great bulk of these curves show no approach to normality. The values of β_1, β_2 range from points on the B-line down to infinity, the distributions contain concentrated blocks, U-shaped curves, J-shaped curves, rectangles, trapezoid-like forms and every variety of skewness in doubly limited range curves. Only in cases where n is very considerable and ρ is neither a positive nor a negative high correlation is there an approximation to the Gaussian. For a series of curves in which β_1 can be 5 and $\beta_2 = 9$,—or both, if we will—ten times these amounts, it is idle to talk about the value of the Gaussian curve ($\beta_1 = 0$, $\beta_2 = 3$) in describing variation. These frequency curves can be actually obtained by experimental sampling, although the process is laborious, and indeed were so obtained in the first place.* They arise from observation and experiment. The remarkable point about them is that they illustrate all the types we have been discussing and justify sharp transitions in algebraic forms by showing that such transitions correspond to actual physical facts arising from experimental statistical data. The whole illustration, details of which will shortly be published, indicates the evil of implicit reliance on a classical theory.

The Gaussian theory of error has, with great weight of authority, been applied to determine significant differences in statistical constants. The theory of the "probable error" must be justified in the case of each statistical constant to which it is applied. Psychologists have been busy discussing the differences found in mental correlations deduced from small samples on the basis of significance judged by the Gaussian theory of probable error. That theory has practically no application, as the "probable error" has really no meaning in the case of the bulk of the samples dealt with. Applications of the theory of probable error in other sciences than psychology to experimental results based on small samples will readily occur to the reader. The conclusions may be correct or incorrect, but they are unquestionably based on an

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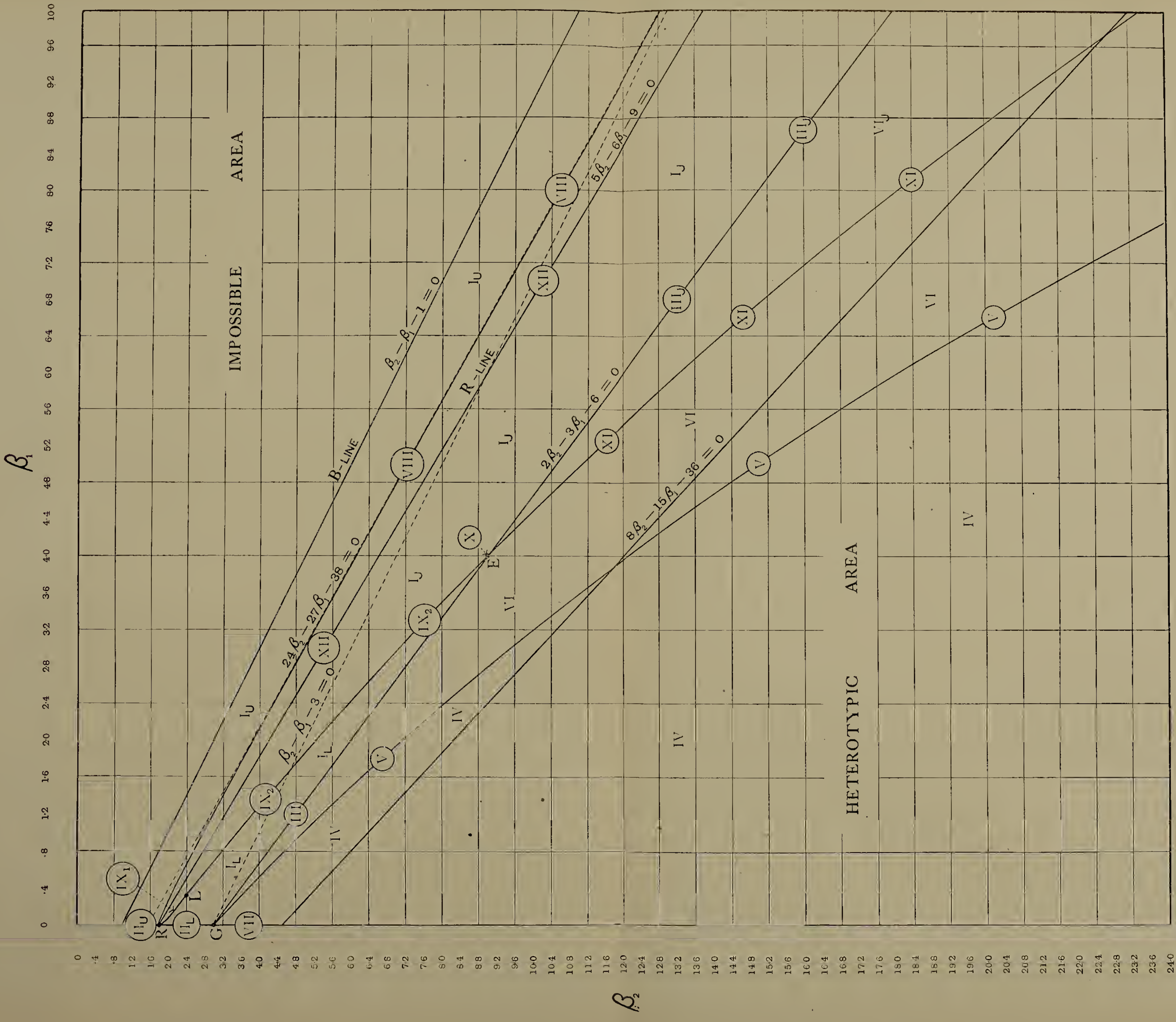
* 'Biometrika,' vol. VI., pp. 305–7.

TYPES OF SKEW FREQUENCY FOR VALUES OF β_1 AND β_2



inflation of the Gaussian point, G, to cover all that may be happening in the whole area of possible β_1, β_2 points in our diagram. It cannot at present be too often emphasised that such inflation is illegitimate, and that, as Dr. ISSERLIS has recently indicated,* the assumption that the distribution curves of statistical constants follow the Gaussian curve is not legitimate, especially in the case of "small samples," which not only for many commercial purposes, *e.g.*, experimental brewing, but in numerous branches of science, *e.g.*, psychology, astronomy, and even physics, are all that economy of money or time permits of being recorded.

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* 'Roy. Soc. Proc.,' A, vol. 92, p. 23.

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[PLATE 2.]

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BY

J. W. NICHOLSON, M.A., D.Sc.,
PROFESSOR OF MATHEMATICS IN THE UNIVERSITY OF LONDON,

AND

T. R. MERTON, D.Sc. (OXON),
LECTURER IN SPECTROSCOPY IN THE UNIVERSITY OF LONDON, KING'S COLLEGE.

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X. *On the Distribution of Intensity in Broadened Spectrum Lines.*

By J. W. Nicholson, *M.A., D.Sc., Professor of Mathematics in the University of London, and* T. R. Merton, *D.Sc.* (*Oxon*), *Lecturer in Spectroscopy in the University of London, King's College.*

Communicated by Prof. A. Fowler, *F.R.S.*

[Plate 2.]

Received February 8,—Read March 9, 1916.

Contents.

(I.) *Introductory.*

It is a curious fact that although our knowledge of the structure of the finest spectrum lines may now be said to rest on a secure theoretical and experimental basis, little is known of the distribution of energy in the broadened spectrum lines which are produced under certain conditions of excitation, or the exact circumstances which control their broadening. The researches of Lord Rayleigh,[*] Michelson,[†] Buisson and Fabry,[‡] and others have shown that in gases at low pressures, when excited by uncondensed electric discharges, the width of the spectrum lines emitted can be accounted for completely and satisfactorily by the translatory motion of the

---

[*] 'Scientific Papers,' vol. I., p. 183; 'Phil. Mag.,' 29, p. 274, 1915.

[†] 'Phil. Mag.,' 34, p. 280, 1892; 'Astrophys. Journ.,' 3, p. 251, 1896.

[‡] 'Journ. de Physique,' vol. 2, p. 442, 1912.

[Published, June 28, 1916.

radiating particles, in accordance with DOPPLER's principle. Measurements of the width of such lines are carried out with the interferometer, the measurement consisting of a determination of the limiting order of interference at which fringes can be seen. This limiting order of interference is given by the equation $N = K (M/T)^{1/2}$ where N is the limiting order of interference, M the mass of the luminous particle in terms of the hydrogen atom, T the absolute temperature and K a constant. This equation is derived from a consideration of the Doppler effect produced by a distribution of the velocities of the radiating particles in accordance with MAXWELL's law, and its experimental verification by BUISSON and FABRY shows not only that under the conditions specified the widths of the lines are completely accounted for, but also that the distribution of intensity in the lines is given by the well-known probability law. Under these conditions it is further shown that the limiting order of interference is constant for all lines and all series of the same element. Thus the same value of N is found for the helium and the parhelium series, and in the same manner for the Balmer series and lines of the secondary spectrum of hydrogen.

With any departure from the specified conditions of low pressure and excitation by uncondensed electric discharge the law breaks down, and the lines broaden in an apparently anomalous manner. The characteristics which lead RYDBERG to adopt the terms diffuse and sharp series appear, the higher members of a series undergoing the greater degree of broadening. Matters are complicated by the fact that the broadening is in many cases unsymmetrical, and in addition we must take into account the fact pointed out by ROYDS,* that different members of the same series may be unsymmetrically broadened in opposite directions. Thus in the case of the first subordinate "triplet" series of barium, the members consisting of triplet and satellites at λλ 5819–5424 are all unsymmetrically broadened towards the red, whilst the members of the succeeding triplet (and satellites) and λλ 4493–4264 are unsymmetrically broadened towards the violet. ROYDS shows that similar phenomena occur in the spectra of calcium and strontium, and points out the importance of the phenomena in relation to the pressure shifts of the lines in question. There can be no doubt of the intimate relation between the direction of the asymmetry and the pressure shift, since it has been shown by ST. JOHN and WARE, FABRY and BUISSON,† and by GALE and ADAMS‡ that iron lines which broaden unsymmetrically towards the red are displaced by pressure towards the red, whilst lines which are unsymmetrically broadened towards the violet are displaced by pressure towards the violet. It is well known that broadening of spectrum lines can be produced either by an increase of the pressure of the luminous gas or by the use of highly condensed discharges as a means of excitation, and although the two conditions are different

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* 'Astrophys. Journ.,' 41, p. 154, 1915.

† 'Astrophys. Journ.,' 36, p. 14, 1912; 31, p. 111, 1910.

‡ 'Astrophys. Journ.,' 37, p. 391, 1913.

the phenomena of broadening which result appear to be similar. In a previous investigation it has been pointed out by one of the authors that from a consideration of the general characteristics of the broadening it appears difficult to refer the phenomena to the movements of the luminous particles as a whole, but rather that effects more intimately connected with the problem of radiation must be concerned. A recent suggestion by STARK[*] as to the cause of the broadening appears to be in harmony with the experimental results at present available.

(II.) *The Stark Effect in Relation to the Broadening of Spectrum Lines.*

STARK[†] has found that when a luminous source is placed in a powerful electric field the radiations are resolved into components in a manner analogous to the Zeeman effect in a magnetic field. The separation of the components in an electric field appears to be related in some way to the atomic weight of the element, the greatest effect being observed in the case of the Balmer series of hydrogen, and the diffuse series of helium. The separation is of another order of magnitude to the corresponding magnetic separation. Thus at $\lambda = 4000$ Å.U. the separation of the outer components of a normal Zeeman triplet in a field of 30,000 Gauss is about 0·5 Å.U., whilst for the hydrogen line H_γ in an electric field of 30,000 volts $\times$ cm.$^{-1}$, the outermost components are separated by 13·0 Å.U. STARK considers that the broadening of spectrum lines at high pressures and under powerful conditions of electrical excitation is intimately connected with the electrical resolution of the lines, being in fact due to the electric effect of neighbouring atoms on the luminous particle. The phenomena appear to be strictly analogous. STARK also points out that the electrical separation of the components increases with the term number in a series, just as the broadening also increases. The electrical separation is greatest for lines of diffuse series, which also undergo the greatest broadening. Further, lines in the spectra of helium and lithium which are unsymmetrically broadened are also unsymmetrically resolved in the electric field.[‡]

It is evident that in order to obtain further evidence it is necessary to determine experimentally the distribution of intensity in the broadened spectrum lines, since we may predict (on this view) from the separation and intensity of the components in an electric field, the distribution of intensity to be expected in the broadened spectrum lines. In a previous communication[§] a method of investigating the distribution of intensity in broadened spectrum lines was described, and it was shown that the results

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[*] 'Elektrische Spectralanalyse Chemischer Atome,' 1914. See also 'Ann. der Phys.,' No. 18, p. 193, 1915, in which the latest results for the Balmer series of hydrogen are given.

[†] *Loc. cit.* A valuable discussion of the subject has recently been published by FULCHER ('Astrophys. Journ.,' 41, p. 359, 1915).

[‡] Reference may be made to the recent work of A. J. DEMPSTER, 'Ann. der Phys.,' 47, p. 791, 1915, who has investigated the breadth of spectrum lines with the interferometer, a method which the writers consider to be unsuitable for reasons given below.

[§] 'Roy. Soc. Proc.,' A 92, p. 322 (1916).

obtained for the hydrogen lines H_α, H_β, and H_γ were qualitatively in accordance with the intensity distribution to be expected on the view that the electric field of neighbouring atoms was responsible for the broadening. The present investigation is concerned with the quantitative determination of the distribution of intensity in broadened spectrum lines, with the view of throwing some further light on the nature of the broadening and the circumstances which control it.

(III.) *The Methods of Measurement.*

It is at once evident from the complex nature of the phenomena that a measurement of the limiting order of interference at which fringes can be seen for the broadened lines will be of little value in determining the intensity distribution. If the intensity distribution could be exactly predicted on theoretical grounds, it might be possible to verify the theory by measurements with the interferometer, but even in this case serious difficulties might arise if the intensity distribution curve were not of some simple form. In a recent investigation KING and KOCH* have described a method of investigating the structure of spectrum lines. The method adopted by these investigators consists in photographing the spectrum under a high dispersion, and in obtaining a curve relating the density of the image on the photographic plate to the wave-length. This is accomplished by causing the plate to move slowly in front of a slit through which light from a constant source is passed, and by continuously recording the resulting changes in the intensity of this light by a method involving the use of the photo-electric cell. The method has yielded valuable results in the study of the variation in the character of spectrum lines under different conditions of excitation, but it would appear difficult to employ a method of this kind to determine the quantitative intensity distribution in the lines on account of the eccentric and somewhat anomalous relations which determine the form and density of photographic images. In adopting a photographic method for quantitative investigation the following phenomena have to be taken into account:—

(I.) There is no linear relation, and indeed no very definite relation, between the density of the image on a photographic plate and either the intensity of the light which produces the image or the duration of the exposure. The relation varies with different brands of plate and is affected by the chemical treatment of the plate in developing the image. An extreme case occurs when the image becomes solarized, or over-exposed to such a degree that it is no longer capable of development, a phenomenon well known to spectroscopists as the cause of the spurious reversal of spectrum lines.

(II.) The product of the intensity of the light by the time of exposure does not produce a constant value of the density of the photographic image, that is to say, a

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* 'Astrophys. Journ.,' 39, p. 213, 1914.

different density is obtained by doubling the intensity of the light and halving the time of exposure.

(III.) The sensibility of the photographic plate varies for different wave-lengths. This, of course, depends on the particular kind of plate used, but may be neglected in the investigation of broadened emission lines, since the sensibility of the plate may be taken as constant over the short range of wave-length covered.

(IV.) Irradiation, or spreading of the image on the photographic plate, which has recently been the subject of a quantitative investigation by TUGMAN.* Owing to the scattering of light by the grain of the plate the size of a photographic image increases with the time of exposure or the intensity of the light.

It is therefore evident that if quantitative measurements are to be made by a photographic method, the method adopted must comply with the principle,† that two sources of light or two regions of illumination can only be considered to be of equal intensity when they produce the same degree of density in the same time on portions of the same photographic plate. It is believed that the method adopted in the present investigation fulfils these conditions and is independent of the eccentricities of the photographic plate.

An accurate wedge of neutral-tinted glass, cemented to a similar wedge of clear glass so as to form a plane parallel plate, was mounted immediately in front of the slit of a spectroscope, in the manner commonly used for determining the sensibility curves of photographic plates. Under these conditions the spectrum of a discontinuous source thrown on to the slit through the neutral wedge is seen to consist of lines which are bright at one end, corresponding to the thin end of the wedge, and gradually fade off towards the region corresponding to the thick end of the wedge. The apparent length of a line depends on its intensity, and the relative intensity of two adjacent lines can be determined by measuring the lengths at which they can just be seen. Since in broadened spectrum lines the intensity, generally speaking, falls off more or less regularly from the maximum of intensity, a broadened line appears, with the arrangement described, as a wedge, the apex of which corresponds to the point of maximum intensity. By a measurement of the shape of the photographed image of such a wedge, it is possible to calculate the distribution of intensity in the broadened line. It is only necessary to pick out points of any convenient density which can be recognised, and to measure their height from the base of the wedge. The method therefore conforms with the conditions that have been laid down, and is independent of the eccentricities of the particular plate used or its subsequent treatment. Since the density which can be most easily recognised is small, it is evident that the results will not be vitiated by irradiation provided that the spreading due to irradiation from the centre of the base of the wedge is small in comparison

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* 'Astrophys. Journ.,' 42, p. 331, 1915.

† *Cf.* HOUSTOUN, 'Roy. Soc. Edinburgh Proc.,' 31, p. 521; 1911.

with the total width of the base. It is therefore necessary that the dispersion of the spectroscope should be sufficiently great in relation to the width of the lines. In the present investigation the lines measured have been of such a breadth that this condition is amply fulfilled, and, moreover, the photographs show that this is the case. At the maximum in the base of the wedge the image is spread out. If, however, the dispersion of the spectroscope is sufficiently great this spreading is no longer visible at the edges of the base of the wedge. An exaggerated drawing of the effect of irradiation on the wedges is shown in fig. 1. In "A" the effect of irradiation is seen at S, but at P and Q, which represent the boundary of the wedge and the "recognisable density," the effect is no longer visible. In "B" it is evident that the effect of irradiation is not eliminated, and that a higher dispersion must be employed if reliable measurements are to be made for the line in question.

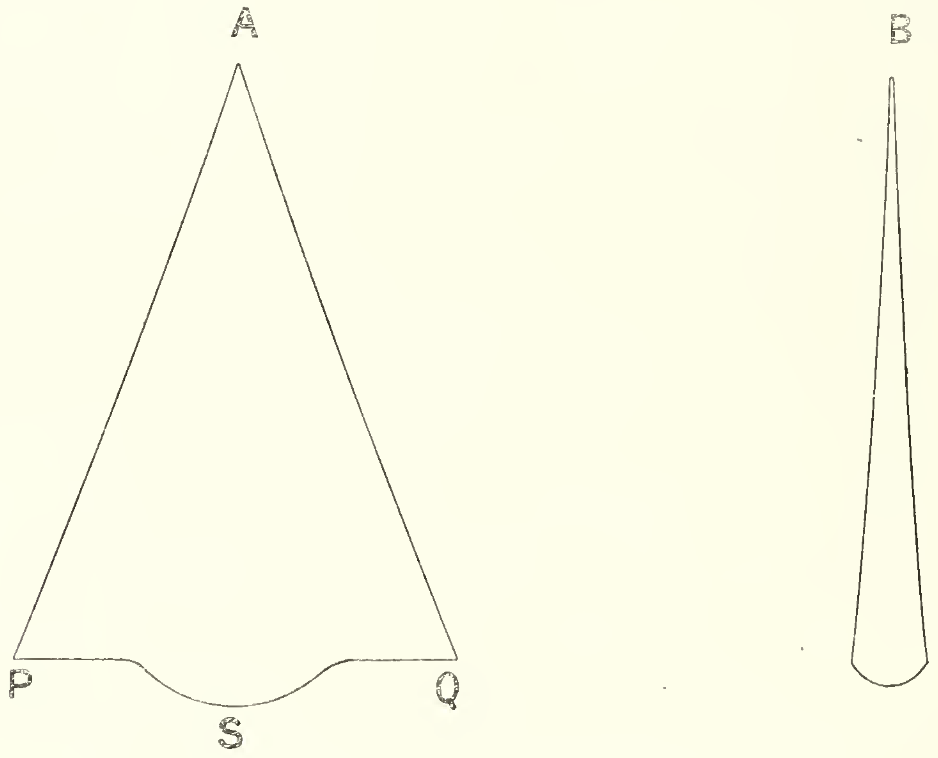

Fig. 1.

(IV.) *Experimental.*

For the production of the spectra investigated condensed discharges were employed from an induction coil capable of giving a ten-inch spark in air, and in parallel with a condenser having a capacity of 0·0025 microfarad. In the case of hydrogen the condensed discharges were passed between aluminium or platinum points in a glass vessel containing hydrogen at atmospheric pressure. In the case of helium a vacuum tube containing the gas at a pressure estimated at somewhat above a millimetre of mercury was employed, and in this case a spark gap was put into the circuit. The spectrum lines produced under these conditions are of such a breadth that the dispersion of a single prism spectrograph was found to be sufficient. The spectrograph consisted of a large model constant deviation spectroscope by Hilger with a camera attachment. The neutral wedge, which was supplied by the same firm, was fastened on to a diaphragm which was fitted in grooves immediately in front of the slit. The slit width used was 0·025 mm. The width of the slit might necessitate a correction in the interpretation of the photographs, but since in the present case the greatest correction would be less than one per cent. of the width of the base of the wedge, it may for the present purpose be neglected. The curvature of the spectrum lines obtained with prism spectrographs has also been considered as a possible source of error, but this also was found to be negligible over the length of slit in use.

The greatest care was taken to ensure the even illumination of the slit, since this might give rise to serious errors. In the case of vacuum tubes there is no difficulty in ensuring this, and in every case the even illumination of the slit was verified before the wedge was put into position. In the case of the spark discharges through hydrogen at atmospheric pressure, the light was concentrated on to the slit by means of a sphero-cylindrical condenser, and in some cases a piece of ground glass was interposed as a further precaution. WRATTEN and WAINWRIGHT'S panchromatic were used, and were in some cases intensified with mercuric bromide and sodium sulphide after fixing. Enlargements were then made on to bromide paper with an enlarging apparatus provided with a Zeiss-Tessar lens, which gives no appreciable distortion over the field required. Since, however, it is in general more easy to work with a negative than a positive, the enlargements were usually carried out in two stages, the first enlargement being made on a Wratten "process" plate or a Paget "half-tone" plate, and the second enlargement on bromide paper.

There remains the personal error in picking out the points of equal density. It is believed that this has been almost entirely eliminated by enlarging the plates through a ruled process screen, the resulting image thus consisting of fine black dots on a white ground. In this way measurements may be easily made by pricking out the last dot visible at a large number of points on the wedge, and subsequently drawing a curve through these points. The extreme dot visible is a very definite point and the drawing of the curves is thus reduced to an almost mechanical process, whereas the recognition of points of equal density on photographs, which have not been prepared in this way, is a matter requiring considerable practice and would undoubtedly be a source of error.

For investigations of a more qualitative nature of the spectrum of lithium, a concave grating spectrograph was used. This instrument consisted of a concave grating of four feet radius of curvature and 20,000 lines to the inch and was mounted according to the arrangement described by EAGLE,* the dispersion being about 10 Å.U. per millimetre.

* 'Astrophys. Journ.,' 31, p. 120, 1910.

(V.) *Theoretical Discussion.*

We may now consider the mathematical interpretation and analysis of the curves obtained.

1. A critical intensity of illumination I_c must exist, such that any intensity smaller than I_c, falling on the plate under the conditions of, and for the time occupied by the exposure, does not produce an effect which can be perceived by the eye. More generally, it would be equally convenient for many purposes to define I_c as the intensity which will produce any specified amount of blackening on the plate, and in the method adopted the amount of blackening specified will represent a dot which is just visible on the enlarged photograph. For, as will appear later, the *loci* of all the points of equal blackening on the plate, due to one component, form similar curves, which only differ in regard to the values of the constants contained in their equations. In determining the general nature of the curve given by any line—and therefore the law of energy distribution in the original image of the slit without incidence on the wedge—this more general conception of I_c is sufficient.

It has been pointed out that the type of broadening of a spectrum line from a gas at low pressure and excited by uncondensed discharges is in accord with discussions based on the theory of probability, following the law

$$I = I_0 e^{-k^2x^2},$$

where I_0 is the intensity at the "centre" of the line—only the case of symmetrical broadening is at present contemplated—and I the intensity at a distance x from the "centre," measured on the wave-length scale, and k a constant.

The assumption has usually been made hitherto that the broadening associated with the condensed discharge also followed the probability law, although the actual amount of broadening is of another order of magnitude under suitable conditions. In fact any other supposition raises difficulties in the physical interpretation according to any suggestions yet put forward. It has never been implied that the effect may not be complex, and due to the joint action of several causes. The broadened line might therefore be formed by the superposition of several probability curves—one arising from each cause—and the resultant intensity law might then cease to be of the usual type, although that type pertained to each of its components. Cases of unsymmetrical broadening can also come into the scope of such a view.

Perhaps the most fundamental result which emerges from a preliminary inspection of the plates is the necessity of abandoning this view. The plates contain photographic records of the intensity curves—showing variation of intensity with wave-length—across certain lines, and although the traces on the plates are not the actual intensity curves, which may be derived from them by a simple formula, yet abrupt changes of curvature in the intensity curves must be accompanied by similar changes on the plates. In other words, the number of separate components, whatever their origin, in a broadened line is represented on the photographic plate, after passage through the wedge, by an equal number of "kinks" in the bounding curve of the darkened patch, provided, of course, that the separations exceed certain limits. A smooth curve, containing no abrupt change of curvature—shown, for example, very definitely in the upper part of the plates for the line H_α (Plate 2)—indicates either a regular law of intensity in the corresponding portion of the original spectral line, or a number of components of very small separation. If in passing across the line, on the wave-length scale, a place was reached where, through the presence of a new and sufficiently separated component, a definitely new law of intensity appeared, a kink would be found on the final plate in the corresponding position. No such kink occurs in the upper portion of the H_α curve, which therefore presents us with one of these alternatives. A first inspection indicates that, for some value of n, $y^n = Ax$ should be a good approximation to the shape of this curve, where A is positive, the axis of x being that of the curve and the origin being at the vertex.

The curvature is away from the axis of x, so that dy/dx increases with x, and d^2y/dx^2 is positive. Thus *n is less than unity.* The curve is, in fact, not unlike the two branches of a semi-cubical parabola, in which $n = \frac{2}{3}$. This property of curvature away from the axis is general throughout the plates, as a casual inspection shows, in all regions where the curvature appears fairly continuous, and therefore determined by only one or by several very close components in the primary broadened line. A single component must therefore ultimately produce, after passage through the wedge, a curve whose equation is at least approximately of the form

$$y^n \propto x,$$

where n is less than unity.

Consider now the curve to be expected for a component satisfying the probability law of intensity.

$$I = I_0 e^{-k^2x^2},$$

where I_0 is the intensity of its centre, and x is the distance of the intensity I from the centre. The wedge diminishes intensity in an exponential manner, and can be defined by a constant ρ such that, if an intensity I_1 falls on the wedge, traverses a thickness η, and emerges as an intensity I_2, $I_2/I_1 = e^{-\rho\eta}$. The intensity I is diminished to I_c, the critical intensity already defined, by a thickness η of wedge given by

$$I_c = Ie^{-\rho\eta} = I_0 e^{-k^2x^2-\rho\eta}.$$

In the figure (fig. 2) ABCD represents the lower surface of the wedge, AB being the intersection of the upper and lower faces, where the thickness diminishes to zero. The shaded area on the lower face of the wedge denotes the final record of the broadened line, whose plane was originally parallel to the lower face and above the upper. Around the boundary of this shaded area the intensity is everywhere I_c, through the combined action of the exponentials of arguments $-k^2x^2$ and $-\rho\eta$ respectively. At X and Y, for example, $\eta = 0$, since no wedge has been traversed, and therefore, if XY = 2D,

$$I_c = I_0 e^{-k^2 D^2}.$$

In fact, X and Y are the traces of the extreme ends (photographically extreme) of the original line, and 2D would be its photographic breadth in the absence of the wedge.

At the apex Z of the shaded area, on the contrary, $x = 0$, for it corresponds to a point on the central axis of the original line. If therefore H is the height of the curve,

$$I_c = I_0 e^{-\rho H \tan \alpha},$$

where α is the angle of the wedge, for $\eta = H \tan \alpha$ for the point Z. If y is the distance of any other point P, on the boundary of the area, from the line AB, and x its distance from the axis OZ of the curve, then x is also the distance from the centre in the original line, of the light affecting P, and $y \tan \alpha$ is the thickness of wedge it has passed through, so that if (x, y) are the co-ordinates of P, referred to an origin at the intersection of base and axis,

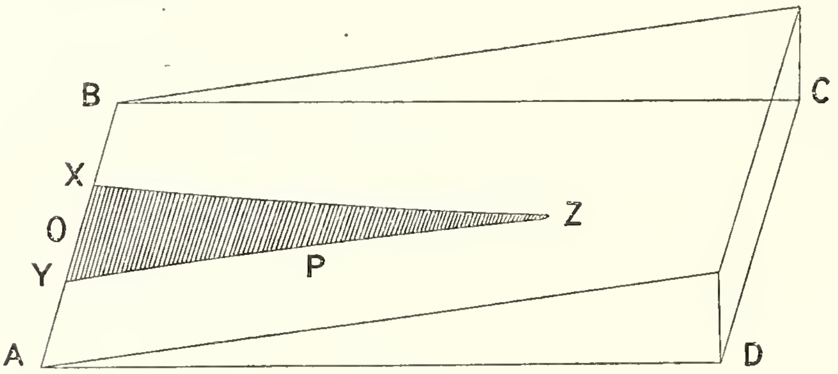

Fig. 2.

$$I_c = I_0 e^{-k^2x^2 - \rho y \tan \alpha},$$

$$= I_0 e^{-k^2 D^2} = I_0 e^{-\rho H \tan \alpha},$$

or

$$k^2x^2 + \rho y \tan \alpha = k^2 D^2 = \rho H \tan \alpha,$$

whence, eliminating k^2,

$$Hx^2 + D^2(y - H) = 0,$$

and the curve on the plate should be parabolic. An obvious change of axes reduces this to

$$y^2/x = D^2/H.$$

But we have already seen that, if the curve is $y^n \propto x$ with this choice of axes, n is less than unity from all the plates. We must conclude that the law of intensity for a single component, or a set of close components, broadened by the condensed discharge, is not a probability law. Whatever it may be, it must be far removed from this, for the curvature of every curve on the plates is diametrically opposite to the requirements of the law. We are therefore not dealing with a case in which the law ceases to be a good approximation, but with something fundamentally different. It is evident that broadening due to a condensed discharge has no relation to the ordinary phenomena, and that the uses made of these phenomena, for example, by Buisson and Fabry, are definitely inapplicable if the conditions of excitation are those of a condensed discharge. This definite conclusion serves to remove several anomalies which have arisen in connection with the application of interference methods to spectral lines, but which need not be classified in detail here.

In view of this failure of the ordinary superposed probability curves towards an explanation of the laws of intensity found in these experiments, it is necessary, before proceeding to a detailed examination of the plates, to give the general theory of the experiment, which from a mathematical point of view is simple. With the notation selected above, let I_0 be the intensity on the axis of a spectral line, and let the law of variation from the axis be $f(x)$. Then the intensity at a distance x along the wave-length scale is $I_0 f(x)/f(0)$. For example, in the preceding case $f(x) = e^{-k^2x^2}$ and $f(0) = 1$. A depth η of wedge reduces this to $I_0 f(x)\, e^{-\rho\eta}/f(0)$.

If H is the height and 2D the breadth of the resulting image on the plate,

$$I_c = I_0 f(D)/f(0) = I_0 e^{-\rho H \tan\alpha}$$

$$= I_0 f(x)\, e^{-\rho y \tan\alpha}/f(0)$$

and

$$f(x)/f(D) = e^{\rho y \tan\alpha}.$$

Using a function $\psi(x)$ instead, where $f(x) = e^{-\psi(x)}$, as being more convenient for calculations, equally general, and more suited to the physical necessity for an exponential type of law

$$\psi(D) - \psi(0) = \rho H \tan\alpha = \psi(x) - \psi(0) + \rho y \tan\alpha.$$

Referring the curve to new axes at its vertex, as in the case already discussed, transferring the origin through a distance H, reversing the axis of y, and finally, interchanging the axes of x and y, we obtain

$$\psi(y) = \rho x \tan\alpha,$$

and the law of intensity denoted by ψ can be found if the equation of the curve on the plate is determined. For example, if the photograph has the equation

$$y^n/x = \text{constant}.$$

where n is a definite number, $\psi(y) \propto y^n$, and $f(x) = e^{-\psi(x)} = e^{-qx^n}$, where q is constant. The law of intensity in the original line is therefore

$$\mathrm{I} = \mathrm{I}_0 e^{-qx^n},$$

being the probability curve when the final curve is a parabola. A case of obvious interest is that of an ordinary exponential distribution of intensity

$$\mathrm{I} = \mathrm{I}_0 e^{-qx},$$

where q is constant, in the original line. The equation to the photograph would then be

$$qy = \rho x \tan \alpha,$$

so that it becomes a straight line, from which the value of q could be measured at once when the optical properties of the wedge, defining ρ and α, are known. This equation, of course, like those preceding, applies to one side of the photograph only, the other side being the optical image of the first in the axis of the photograph. For example, the present case would present, as the complete boundary, two straight lines intersecting at the apex of the curve, and inclined at an angle closely given by $2\rho\alpha/q$, where α is the small angle of the wedge.

If the law were partly exponential and partly of the probability type, or $\mathrm{I} = \mathrm{I}_0 \exp(-k^2x^2 - qx)$, where k^2 and q are *positive* constants, the graph on the plate would become

$$k^2y^2 + qy = \rho x \tan \alpha,$$

and it is easily demonstrated that this is a parabola exactly similar—and, in fact, equal—to the parabola obtained when $q = 0$, but shifted on the plate so that its axis has moved parallel to itself. The curve is therefore still symmetrical about its axis and curved *towards* it, so that this mixed law is incapable of explaining the characteristics of the photographs even on general grounds. In fact, the constant q has no influence on the radius of curvature. It would, however, have an influence if the law with which the simple exponential is combined were anything other than the law of probability.

This lack of influence of q, however, only applies to corresponding points, and in order to avoid misconception, a more complete account is necessary, for the curve as seen on the plate would actually appear flatter and be of smaller extent. At the same time it undergoes a sudden change of curvature at the vertex. In the annexed figure (fig. 3) the dotted curve is the parabola which would be obtained when $q = 0$. The other parabola ABCDE is the shifted parabola obtained when q is not zero, as explained already. But only the portion ABC appears on the plate, for the axis OX cannot be disturbed by the presence of the new exponential factor, which must also lessen the height of the curve to the value CX. What is actually seen is ABC and its image in OX, or the shaded area in the figure bounded by two arcs of parabolas whose vertices are not at C, which therefore exhibits a sharp peak. In fact, the original dotted parabola really consists of arcs of two parabolas which happen to be coincident when $q = 0$, and the analysis always applies only to one side of the axis, as was emphasised earlier.

The interaction of two laws of energy distribution in a line, one being the simple exponential law, could therefore explain the peaked appearance at the vertices of the photographs, but it is incapable of explaining the nature of the curvature if the other law is that of probability. It is evident on inspection of corresponding points why one curve is flatter than the other, although the parabolas are equal.

On the supposition that H_α is not complex in these experiments (a supposition which is ultimately disproved), it is a matter of practical importance to isolate the simple exponential law which may be superposed on any other, and although the curves appear, in their continuous parts, to follow a law of the form $y^n \propto x$, we must assume, in view of their peaked nature, that the best representation in terms of one component will be

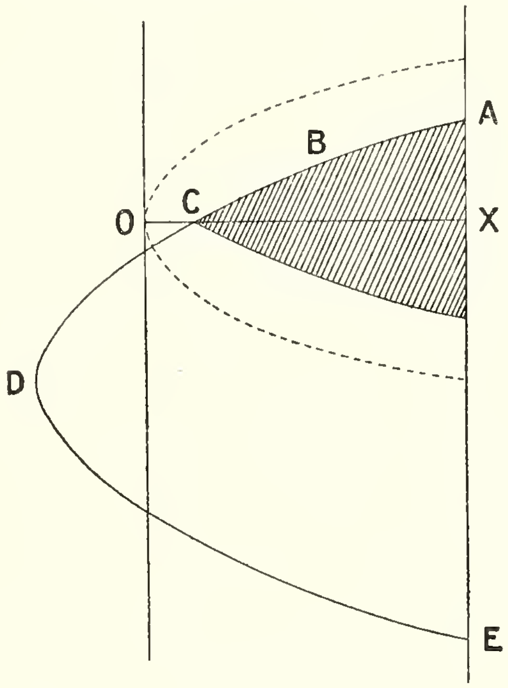

Fig. 3.

$$y^n + \delta y = \beta x,$$

where δ and β are constants, n being less than unity. The curves, when of continuous curvature, are obviously so nearly straight lines—as, for example, in the upper part of the curves for H_α—that the simple exponential law is evidently the predominant feature, and much analysis is thereby saved. For, as a first approximation, $y = \beta x/\delta$, and the second approximation is easily found to be

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}}.$$

The relation of these constants δ and β to the constants of the energy distribution of the original spectral line may be found as follows:—If the law of intensity distribution is

$$I = I_0 e^{-kx^n - qx},$$

around the maximum at $x = 0$, and if H and 2D are the height and breadth of the photograph,

$$\rho y \tan \alpha + kx^n + qx = kD^n + qD = \rho H \tan \alpha$$

with reference to the old axes. Taking the new axes at the vertex,

$$ky^n + qy = \rho x \tan \alpha.$$

Thus

$$\delta = q/k, \ \beta = \rho \tan \alpha/k$$

and also

$$BH = D^n + D\delta$$

where 2D is the photographic breadth of the original spectral line.

The actual photographs on which measurements have been made were previously magnified in definite ratios. For a magnification m, the equation of the upper portion of such a photograph as those of H_α would become

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}} m^{1-n}.$$

It is necessary to determine whether a unique value of n exists through the photographs of one particular line, permitting the equations of the contours to take this form, in order to decide whether the line has one or more components. H_α is a suitable medium for this determination, and a succeeding section takes up this question.

(VI.) *The Effect of Dispersion.*

When the photographs are magnified on a large scale they all appear unsymmetrically broadened towards the violet. This is the effect to be expected from the fact that the spectrum produced by the prism is not normal, and it is necessary, before a detailed analysis of the photographs can be made, to calculate the asymmetry due to this cause and to compare it with the actual effect observed. A complete account of this problem is given below in connection with the best magnified photograph obtained for H_α. The dispersion on the original plate, before magnification, was known to be given very accurately by the formula

$$\lambda = \lambda_0 + C/(n + n_0)$$

where $\lambda_0 = 2257{\cdot}5$, $C = 116{,}802{\cdot}9$, λ is in Å.U., and $n + n_0$ is in millimetres of the scale. The scale reading for the centre of the pattern of $H\alpha$, $\lambda = 6563$, is, therefore, on the original plate

$$n + n_0 = 116{,}802{\cdot}9/(6563 - 2257{\cdot}5) = 27{\cdot}13 \text{ mm.}$$

We shall suppose provisionally that the law of energy distribution round the central component of the original line is the same on both sides, so that with equality of dispersion, the final pattern would be symmetrical. Let $6563 \pm \alpha$ be the limiting wave-lengths which can just be seen on this pattern at the thin end of the wedge. Then the corresponding scale readings at the ends of the pattern are

$$n+n_0 = \mathrm{C}/(6563-\lambda_0 \pm \alpha),$$

or

$$27{\cdot}13 \mp \mathrm{C}\alpha\,(6563-\lambda_0)^{-2}+\mathrm{C}\alpha^2\,(6563-\lambda_0)^{-3}.$$

The length of the red end of the pattern is $\alpha\mathrm{C}\,(6563-\lambda_0)^{-2}-\alpha^2\mathrm{C}\,(6563-\lambda_0)^{-3}$ and of the violet end, $\alpha\mathrm{C}\,(6563-\lambda_0)^{-2}+\alpha^2\mathrm{C}\,(6563-\lambda_0)^{-3}$, neglecting higher powers. The difference is $2\alpha^2\mathrm{C}\,(6563-\lambda_0)^{-3}$ and the total length $2\alpha\mathrm{C}\,(6563-\lambda_0)^{-2}$. If this total length is d, the difference becomes $\alpha d/(6563-\lambda_0)$ or $(6563-\lambda_0)\,d^2/2\mathrm{C}$. By calculation, this becomes $d^2/54{\cdot}26$ in the present case, where d is in millimetres.

This calculation is valid not only for the extreme thin end of the wedge, but for any thickness of wedge, for both the wave-lengths, $6563 \pm \alpha$, have the same original intensity, and therefore disappear on the photograph at equal heights, corresponding to equal thicknesses of wedge traversed. We may now apply this result to one of the photographs of H_α (Plate 2).*

This plate has been reproduced by the half-tone process, which reproduces the dotted effect used in determining the boundary of the curve. The vertex of the curve* is well defined, and the axis must be parallel to the original slit, and can be determined precisely. The magnification in this case was × 33, and the breadth of the curve at its base is 59·0 mm. The breadth of the original plate was therefore 59/33 = 1·7879 mm. Thus,

$$d = 1{\cdot}7879 \text{ mm.} = v+r$$

where v and r are the breadths of the violet and red ends.

Also

$$v-r = d^2/54{\cdot}26 = 0{\cdot}0589 \text{ mm.}$$

The difference on the photograph magnified 33 times is 0·0589 × 33 or 1·97 mm., but where, on this photograph, $d = 14$ mm. say, the difference is 1·97/16 or 0·12 mm. and could hardly be observed. Even the magnified curves must therefore look very symmetrical at some distance from the apex, and this is actually the case. An important corollary from this result is that the upper part of the curve can be used to give a geometrical construction for the determination of the axis of the curve. This method has been applied to H_α, to check the supposed position of its axis, with

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* In the reproduction (Plate 2) the whole of the paper is dotted, and the outline cannot therefore be traced exactly. In the original photographs used for measurement, the only dots visible are those which build up the magnified image, thus enabling the boundary to be precisely determined.

very accurate agreement. When the axis was thus verified, measurements of the breadth between the two extreme dots visible laterally were taken at various levels on the height of the curve. It is not thought necessary to give these measurements in detail, and perhaps one example will suffice. The measured distance between the extreme dots at the lower end of the photograph, where it is broadest, is 59·0 mm. as stated already, and the violet and red portions have breadths 30·5 and 28·5, measuring on either side of the axis. This difference is 2·0 mm. against the theoretical value 1·97. This agreement, typical of the agreement throughout, is a convincing proof that the broadened H_α is, in its energy distribution, *absolutely symmetrical* about its centre, and that the apparent asymmetry—only evident to the eye on the magnified photographs—is entirely due to the fact that the prismatic spectrum is not normal.

This is the second fundamental result of the work—that *the broadening of* H_α *under the condensed discharge is an absolutely symmetrical one.*

To a high order of approximation, inequality of dispersion lengthens the breadth of the violet and shortens that of the red to an equal extent, so that their sum is the breadth of the curve with a dispersion uniformly equal to that at λ6563. To draw a graph of the symmetrical curve for uniform dispersion, therefore, we merely require to measure the total breadth of the photograph for various heights, and plotting half total breadth against height, we obtain one side of the curve for uniform dispersion. Now the total height, from base to apex, of the H_α curve in question, is 192 mm., and the excess of breadth of the violet over the red end, even at the base, is only 2 mm. in a total breadth of 59 mm. The alteration in shape caused by this correction is therefore very slight, and can produce no appreciable tendency to a parabolic form on either side. The previous conclusion as to the absence of a probability law remains, therefore, unaffected.

(VII.) *The Complex Structure of* H_α *when Excited by Condensed Discharges.*

The symmetry of H_α being established, the two alternatives still remain. H_α may be a single component symmetrically broadened—to disprove this supposition is our immediate object—or a set of symmetrically-arranged but close components, each broadened in a symmetrical manner. The theory of this second case has not yet been given, and in assuming that it is a possible interpretation of the photographs, we are anticipating the theory given later. Confining attention for the present to the first alternative, and recalling that any law must, for physical reasons in the case of emission, be of some exponential type, and from the appearance of the curves, mainly a linear exponential, we have the formula, for magnification m,

$$y = \frac{\beta x}{\delta} - \frac{\beta^n x^n}{\delta^{n+1}} m^{1-n},$$

n being less than unity, and δ large and positive. The first condition, as regards n, is necessary to secure the curvature in the right direction. Now this could also be secured mathematically if n were greater than unity, and δ negative, but this case is a physical absurdity, for it signifies a law of intensity in the original light of the form

$$\mathrm{I} = \mathrm{I}_0 e^{-a^2x+b^2x^n},$$

where a and b are real constants, and $n > 1$. The intensity would then begin by decreasing from the centre, and finally *increasing* without limit. This is contrary to experience and also to physical possibility. But it is unfortunately the case to which we are led when an attempt is made to apply the formula to the curve for H_a. The following numerical example from one photograph makes this clear, and indicates at the same time that small changes in the measurements would not reverse the conclusion.

β/δ at the vertex may be obtained with accuracy as the initial slope, and is found to be 0·0573, by a construction involving the result as a ratio of two large distances. The following points are on the curve, and distances are expressed in millimetres.

$$\left.\begin{array}{l} x = 162{\cdot}5 \\ y = 16{\cdot}0 \end{array}\right\}, \qquad \left.\begin{array}{l} x = 192{\cdot}0 \\ y = 29{\cdot}5 \end{array}\right\},$$

and applying the formula we find,

$$n = 5{\cdot}97, \qquad \delta/m^{n-1} = -0{\cdot}870.$$

The mixed law,

$$\mathrm{I} = \mathrm{I}_0 \, e^{-qx-kx^n},$$

can therefore give no interpretation of the curves, and a more general conclusion is possible. For the result may be extended in the same way to a law compounded of three, when further measurements are made. It is not thought necessary to reproduce the calculations to this effect. The conclusion, therefore, appears inevitable that the details of the shape, and even the general form, of the curve H_a, are not compatible with the view that H_a contains only one component broadened, perhaps by various agencies, simultaneously by any physically possible exponential laws, the total argument of the exponential being *additive* in the complete law. We are compelled to seek an explanation of the curve in terms of several components whose individual curves are superposed, and are led directly to the Stark effect as the foundation of the whole phenomenon. Several qualitative reasons have already been advanced in favour of this hypothesis, and it now appears further that a quantitative study of the curves necessitates the same hypothesis. For if several components are to be admitted, only the Stark effect seems capable of providing them, and the fact that they must be symmetrical in H_a enhances this conclusion. The components are conspicuous in $\mathrm{H}\beta$

and some other cases, but in H_α a closer scrutiny is required to reveal them. In order to cover such cases the theoretical discussion has been made somewhat complete.

(VIII.) *General Theory of a Symmetrically Compound Line.*

If H_α has close components, the law of attenuation of each component from its maximum is now certainly that of the simple exponential,

$$I = I_0 e^{-qx},$$

for the whole of the curve for H_α is very close to a straight line, and for nearly half its length is almost entirely straight. Afterwards it broadens convex to its axis, but not rapidly, and although so irregularly as to invalidate attempts to interpret it by a single exponential of any possible argument, the curvature is nevertheless at *every* point away from the axis. Several close components with somewhat different rates of attenuation, but with axes nearly coincident, are at once suggested, and will be shown to provide a complete explanation of these peculiarities. No other exponential arrangement appears capable of doing so.

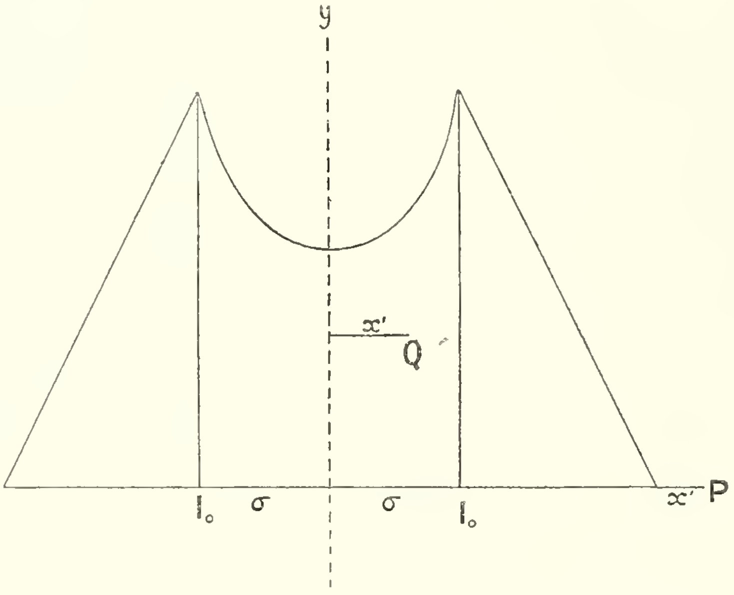

Fig. 4.

As the components of H_α are symmetrically arranged, we consider first the effect of a pair of equal components separated by an interval 2σ.

Let I_0 (fig. 4) be the axial intensity of either. A dotted line in the figure is midway between their axes, and is taken as the axis of y. Then at a point P of co-ordinate x outside both axes the intensity is $I = I_0 e^{-q(x-\sigma)} + I_0 e^{-q(x+\sigma)} = 2I_0 \cosh q\sigma e^{-qx}$ and this would be produced by a *single* line of axial intensity $2I_0 \cosh q\sigma$ midway between. But at a point Q (x') between the axes the intensity is

$$I = I_0 e^{-q(\sigma+x')} + I_0 e^{-q(\sigma-x')} = 2I_0 e^{-q\sigma} \cosh qx',$$

following a different law. A wedge whose length lies along y would produce a curve of critical intensity I_c which, outside both axes, would have an equation

$$I_c = 2I_0 \cosh q\sigma e^{-qx-\rho y \tan \alpha}$$

or

$$\rho y \tan \alpha + qx = \log_e (2I_0 \cosh q\sigma / I_c)$$

and be straight. But between the axes the equation is

$$I_c = 2I_0 \cosh qx \,.\, e^{-q\sigma-\rho y \tan \alpha}$$

or

$$\rho y \tan \alpha = \log_e (2I_0/I_c) - q\sigma + \log_e \cosh qx,$$

which is curved. We can verify at once from these equations that dy/dx is discontinuous and changes sign when $x = \sigma$, and that the form of the curve of intensity I_c is as shown in the figure (fig. 4). The summits of these curves, however, are not the summits which the separate components would individually show. The upper parts of the photographs of H_β indicate this appearance very precisely, so that the strongest components of H_β form a symmetrical pair.

Before proceeding to the effect of superposition of such pairs, together with a possible central component, we must prove a very general theorem. The main characteristic of all the curves which have been photographed, not only of hydrogen lines, but of helium and lithium, is that they contain no point at which the curvature is towards the axis. In other words, if y is measured as in the last figure, d^2y/dx^2 is always positive whatever the sign of dy/dx. Apparently the only exponential arrangement which is physically possible and possesses this property in general is the class of curves dealt with in the theorem. A proof of this statement would occupy some space, and we therefore merely prove that this class has the necessary property.

Consider a set of lines, n in number, with any rates of attenuation $q_1, q_2, \ldots, q_n$, whose axes are coincident. Their central intensities are $I_1, I_2, \ldots, I_n$. If $\kappa = \rho \tan \alpha$, the bounding curve of the photograph they produce is given by the equation

$$I_c e^{ky} = \sum_{r=1}^{r=n} I_r e^{-xq_r},$$

when they are all simply exponential. Accordingly, by differentiating twice,

$$\kappa I_c \frac{dy}{dx} e^{ky} = -\sum_1^n I_r q_r e^{-xq_r},$$

$$\kappa^2 I_c \left\{ \left(\frac{dy}{dx}\right)^2 + \frac{1}{\kappa} \frac{d^2y}{dx^2} \right\} e^{ky} = \sum_1^n I_r q_r^2 e^{-xq_r},$$

whence, by eliminating dy/dx and e^{ky}, we derive

$$\sum_1^n \mathrm{I}_r e^{-xq_r} \cdot \sum_1^n \mathrm{I}_r q_r^2 e^{-xq_r} - \left(\sum_1^n \mathrm{I}_r q_r e^{-xq_r}\right)^2 = \kappa \frac{d^2y}{dx^2}\left(\sum_1^n \mathrm{I}_r q_r e^{-xq_r}\right)^2.$$

Let $\lambda_r = \mathrm{I}_r e^{-xq_r}$, so that $\lambda_1, \lambda_2, \ldots, \lambda_n$ are all necessarily positive by physical considerations. Then the sign of d^2y/dx^2 is that of

$$\sum_1^n \lambda_r \cdot \sum_1^n \lambda_r q_r^2 - \left(\sum_1^n \lambda_r q_r\right)^2 = \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} \lambda_r \lambda_s (q_r - q_s)^2.$$

This is a sum of squares with positive coefficients, and is essentially positive for all values of x. Thus d^2y/dx^2 is always positive. Even if some of the quantities q_r were positive, this proof would be equally valid, and curves of equal density on the photograph would have d^2y/dx^2 positive at all points.

The curves obtained with any of STARK's resolutions, if the components followed the simple exponential law, would all be included in this class. For they involve a possible central component $\mathrm{I}_0 e^{-qx}$ and pairs of components. A pair at points on the same side of both axes, if of separation 2σ, produces an intensity $2\mathrm{I} \cosh q\sigma e^{-qx}$ at a point x, where $2\mathrm{I} \cosh q\sigma$ is constant. At a point x between the axes the intensity is $\mathrm{I}e^{-q\sigma}(e^{qx}+e^{-qx})$, and the pair is equivalent to two central components, one increasing and the other decreasing. Any Stark resolution is therefore, under this law, equivalent to a set of components whose axes coincide, and the theorem follows.

As already stated, this is the only possible exponential arrangement with the property in question, and this theorem in itself provides a very convincing argument in favour of the suggested theory of broadening, even when a close scrutiny is required to reveal the components.

Let now a central component be superposed on a symmetrical doublet of separation 2σ. If the suffixes 1 and 2 refer to the component and the doublet, the curve of intensity I_c is, between $x = 0$ and $x = \sigma$,

$$\mathrm{I}_c e^{py \tan \alpha} = \mathrm{I}_1 e^{-q_1 x} + 2\mathrm{I}_2 e^{-q_2 \sigma} \cosh xq_2$$

and, between $x = \sigma$ and $x = \infty$,

$$\mathrm{I}_c e^{py \tan \alpha} = \mathrm{I}_1 e^{-q_1 x} + 2\mathrm{I}_2 e^{-q_2 x} \cosh \sigma q_2.$$

The two branches meet at $x = \sigma$, and the ratio of the two values of dy/dx at $x = \sigma$ is

$$\left\{1 - \frac{2q_2\mathrm{I}_2}{q_1\mathrm{I}_1} \sinh \sigma q_2 \cdot e^{-\sigma(q_2-q_1)}\right\} \Big/ \left\{1 + \frac{2q_2\mathrm{I}_2}{q_1\mathrm{I}_1} \cosh \sigma q_2 \cdot e^{-\sigma(q_2-q_1)}\right\},$$

which is obviously less than unity. It can be negative if I_2 is sufficiently large compared with I_1, and then the curve would have a sharp peak at $x = \sigma$. Otherwise there is only a discontinuity in the slope of the form shown in the figure (fig. 5), the dotted lines being parallel to x and y.

If $q_1 = q_2$, the lower branch is straight.

We may pass at once to the general case of a central component and n doublets symmetrically arranged round it. Between the centre and $x = \sigma_1$, an axis of the first doublet, the intensity curve I_c becomes

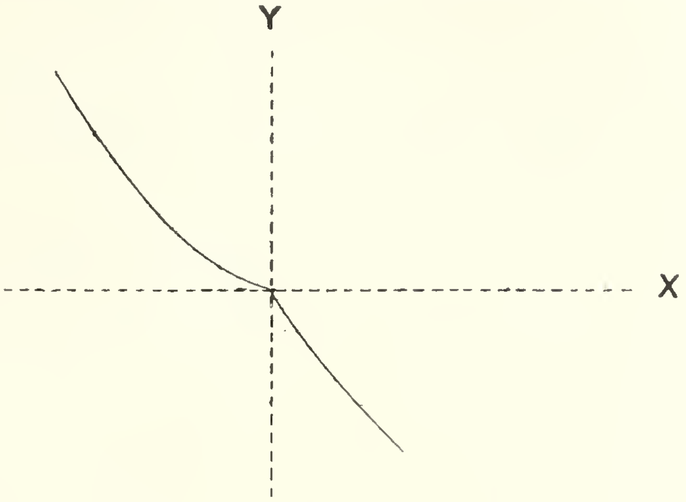

Fig. 5.

$$I_c e^{\rho y \tan \alpha} = I_0 e^{-xq_0} + \sum_1^n 2I_r \cosh xq_r \,.\, e^{-q_r \sigma_r}.$$

Between this axis and one of the second doublet at $x = \sigma_2$,

$$I_c e^{\rho y \tan \alpha} = I_0 e^{-xq_0} + 2I_1 \cosh q_1\sigma_1 \,.\, e^{-xq_1} + \sum_2^n 2I_r \cosh xq_r \,.\, e^{-q_r\sigma_r}.$$

Between $x = \sigma_2$ and $x = \sigma_3$, relating to the third doublet,

$$I_c e^{\rho y \tan \alpha} = I_0 e^{-xq_0} + 2I_1 \cosh q_1\sigma_I \,.\, e^{-xq_1} + 2I_2 \cosh q_2\sigma_2 \,.\, e^{-xq_2} + \sum_3^x 2I_r \cosh xq_r \,.\, e^{-q_r\sigma_r},$$

and so on. In any special case, the branches of the curve may be studied from these equations. The whole curve has discontinuities in dy/dx at $x = \sigma_1, \sigma_2, \ldots, \sigma_n$, and these may be of the form shown above, or actual peaks, such as can be seen in the photographs of H_β which have been taken by this method. Much depends on the relative values of the quantities q for the various components. When a peak occurs, say at $x = \sigma_r$, it is easy to calculate the lowest depth of the curve between $x = \sigma_{r-1}$ and $x = \sigma_r$ before it rises to the peak, and also the rates of slope from the peak, by differentiating the preceding equations.

When there is no previous knowledge of the values of the q's or of the intensities, a complete mathematical analysis of the curve is extremely difficult when there are several components, and this will not be attempted in the present paper in any individual case; but much information can be derived by taking definite cases of the Stark effect and plotting the results which the present wedge should give. This is a more rapid method than direct calculations for determining the essential features which the curve should present under various circumstances.

In his most recent paper, Stark has given the details of the various components of H_α as follows, although, in view of the difference in the conditions, we must not expect them to appear without serious modification in the present experiments. Under a field of 104,000 volts/cm. Stark finds for H_α:

	No. of component.	Separation (Å.U.).	Intensity.
p components	+3	+11·5	1·2
	+2	+ 8·8	1·1
	+1	+ 6·2	1·0
	−1	− 6·2	1·0
	−2	− 8·8	1·1
	−3	−11·5	1·2
s components	+1	− 2·6	1
	0	0	2·6
	−1	− 2·6	1

Now if a broadened line has an intensity I at its centre, and follows the simple exponential law, the quantity of energy in it is proportional to

$$\mathrm{I}\int_0^\infty e^{-qx}\,dx = \mathrm{I}/q.$$

Stark's lines are not broad, and intensity in such a case is rather a measure of contained energy than of central brightness, whatever the mode of measurement. The last column of Stark's table, therefore, may be taken as a measure of I/q where I is the central brightness of a line. The distinction is immaterial if q is the same for each component.

Now for the wedge adopted, it was known that if an intensity I_1 passing through emerged as I_2, and if

$$\log_{10}(\mathrm{I}_1/\mathrm{I}_2) = \mathrm{X},$$

then $\mathrm{X} = 0{\cdot}2+0{\cdot}4y$, where y was the distance from the thin end, which was not indefinitely thin. But

$$\mathrm{I}_2 = \mathrm{I}_1 e^{-\rho y \tan\alpha} = \mathrm{I}_1 \,.\, 10^{-\rho y \tan\alpha \,.\, \log_{10} e},$$

and therefore

$$\rho \tan\alpha = 0{\cdot}4/\log_{10} e = 0{\cdot}922,$$

or practically unity.

The form of the curve for H_α, and in fact of all curves obtained, is not consistent with the supposition that q is the same for all components. There are two alternatives to consider in a very simple proof. If the separations are very minute, all points on the contour not between two components—or in other words all points except very close to the vertex, are outside all the component axes, and if q were constant throughout, all the boundary beyond a small distance from the vertex would take the form

$$I_c e^{\rho y \tan \alpha} = \left(I_0 + 2 \sum_{r=1}^{4} I_r \cosh q\sigma_r\right) e^{-qx},$$

and be entirely straight. This is not the case. In the second place, if the separations were comparable with STARK'S, the initial part of the curve would be

$$I_c e^{\rho y \tan \alpha} = I_0 e^{-qx} + 2 \sum_{r=1}^{4} I_r \cosh xq \,.\, e^{-q\sigma_r},$$

and $dy/dx = -q/\rho \tan \alpha$ at $x = 0$, whereas near $y = 0$ in the final part of the curve outside all the component axes, the slope is again $-q/\rho \tan \alpha$. The initial and final slopes should therefore be equal whatever the nature of the kinks. This does not occur, and we must therefore conclude that *the rates of attenuation of components are different.* The same conclusion can be deduced in other ways from the curves. The rate of attenuation of the central component is given by the initial slope in all cases, if the separations are not so extremely small as to make this an indefinite quantity. From the photographs of H_α in the present experiments we find as the mean of several measurements,

$$\rho \tan \alpha / q = 0{\cdot}057,$$

whence $q = 16{\cdot}2$ for the central component, since $\rho \tan \alpha = 0{\cdot}922$.

It has been taken for granted that the separations in H_α are not minute, in accordance with later work. The detailed description of H_α will follow, our present object being the derivation of results applicable in general to the whole series of curves, with H_α as a convenient illustration.

The values of q decrease as the separation of the components increases. This can be deduced from the fact that the final slope of all the curves to the axis of x (the base of the photograph) is smaller than the initial slope. For the final slope is derived from the final branch,

$$I_c e^{\rho y \tan \alpha} = I_0 e^{-xq_0} + 2 \sum_{r=1}^{n} 2I_n \cosh q_n\sigma_n \,.\, e^{-xq_n},$$

and

$$-\rho \tan \alpha \frac{dy}{dx} = \left\{ I_0 q_0 e^{-xq_0} + 2 \sum_{1}^{n} I_n q_n \cosh q_n\sigma_n \,.\, e^{-xq_n} \right\} \Big/ \left\{ I_0 e^{-xq_0} + 2 \sum_{1}^{n} I_n \cosh q_n\sigma_n e^{-xq_n} \right\},$$

or if $I_n/q_n = E$, the measure of energy contained in a component determined by STARK'S tabular intensity,

$$-\rho \tan \alpha \frac{dy}{dx} = \left\{ E_0 q_0^2 e^{-xq_0} + 2 \sum_1^n E_n q_n^2 \cosh q_n \sigma_n \, . \, e^{-xq_n} \right\} \Big/ \left\{ E_0 q_0 e^{-xq_0} + 2 \sum_1^n E_n q_n \cosh \sigma_n q_n \, . \, e^{-xq_n} \right\},$$

whereas the initial slope is given by

$$-\rho \tan \alpha \, dy/dx = q_0.$$

The difference, which reduces to

$$\left(2 \sum_1^n q_n (q_0 - q_n) E_n \cosh q_n \sigma_n e^{-q_n x} \right) \Big/ \left\{ E_0 q_0 e^{-xq_0} + 2 \sum_1^n E_n q_n \cosh \sigma_n q_n \, . \, e^{-xq_n} \right\},$$

must be positive, which can only be the case in general if $q_0 > q_n$. Thus *when a line showing the Stark effect is broadened, the components become more diffuse in the order of their separations in general.* Their energy is more spread out, and even if two components have the same tabular intensity in direct methods of resolution as fine lines, their heights on the photographs by the present method of the condensed discharge may be very different. For these heights are not determined by the energies in the components, but by their central intensities, which are proportional to their rates of attenuation q. It is now possible to understand at once the reason for the absence of peaks in the curve for H_α even when the energies of all the components may be strictly comparable with that of the central one. This increase of "spreading" of the components with their distance from the centre is to be expected from the fact that the change in frequency of the radiation from a specified particle depends on the degree of proximity of other charged particles, the distribution of which is subject to variations. If the arrangement of luminous and charged particles were not subject to some probability distribution, we should find sharp components as in STARK'S experiments.

(IX.) *Details of the Components of* H_α.

The theoretical boundary of the curve for H_α, on the basis of STARK'S results, has been plotted for various values of q attached to the different components, in order to discover the dependence of the curve upon these values. For values at all nearly equal, the curve consists of a series of sharp peaks of nearly equal height, separated by deep hollows; and it is evident, therefore, that the decrease in the value of q as the components separate from the central one is rapid. In these circumstances, the kink in the curve loses its peak-like character and becomes a mere protuberance. Moreover its shape for any component ceases to depend to any extent on any other component but the two adjacent, and more particularly the upper one. The illustrative case which has been selected is a fair approximation to the actual case of H_a, and contains both varieties of kinks. It is the upper part of the curve based on STARK's numbers for intensity and separation, magnified in the ratio 33 : 1 from the original theoretical photograph, and with a total height of 198 cm., arbitrarily selected, as the approximate height of the H_a photograph. The initial slope is taken also as that of the photograph, so that $q_0 = 16{\cdot}5$ and $\rho \tan \alpha = 1$. (q_1, q_2) for the first two other components are taken arbitrarily as 5 and 2, and (q_3, q_4) still smaller, so that they have no appreciable effect on the first two kinks.

The figure (fig. 6) exhibits the result of the calculations, the details of which are fairly obvious. The heights of the kinks are calculated and the slopes of the two branches at each. The trough preceding the first kink is calculated as a minimum height on its branch, and other points are plotted from the equations in the ordinary way.

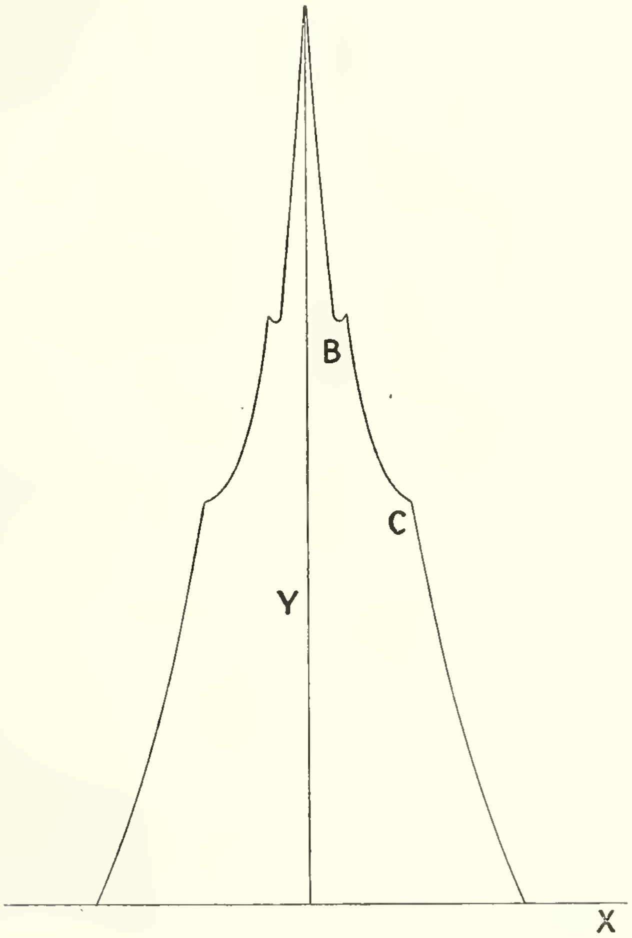

Fig. 6.

STARK gives the central component an intensity 2·6, and the next two an intensity 1 each. These are energy measures, and the central intensities of the broadened components are proportional to $2{\cdot}6q_0$, $5q_1$, $2q_2$, or 42·9, 5, 2 respectively, and are represented by these numbers on a certain scale. The whole height, h, of the curve of intensity I_c is given by

$$I_c e^h = 42{\cdot}9 + 2\,(5e^{-5\sigma_1} + 2e^{-2\sigma_2}),$$

and $h = 198/33 = 6$ mm. on the original photograph, whence I_c is known on the same scale. The separations σ_1, σ_2 are those of STARK reduced to millimetres on the basis 10 Å.U. = 1 mm. valid in these experiments, and become $\sigma_1 = 0{\cdot}26$ mm., $\sigma_2 = 0{\cdot}62$ mm.

The heights of the two kinks are h_1 and h_2, where

$$I_c e^{h_1} = 42{\cdot}9 e^{-16{\cdot}5\sigma_1} + 2\left\{5 \cosh 5\sigma_1 \,.\, e^{-5\sigma_1} + 2 \cosh 2\sigma_1 \,.\, e^{-2\sigma_2}\right\},$$

$$I_c e^{h_2} = 42{\cdot}9 e^{-16{\cdot}5\sigma_2} + 2\left\{5 \cosh 5\sigma_1 \,.\, e^{-5\sigma_2} + 2 \cosh 2\sigma_2 \,.\, e^{-2\sigma_2}\right\}.$$

Multiplication by 33 gives the heights on the enlarged photograph. The values of dy/dx are calculated in a similar way.

In the resulting diagram, the kink at B is still a peak, but its height is very small. Down to the immediate vicinity of B, the curve is hardly distinguishable from a straight line, and its change to B is very abrupt. BC is again practically straight until the vicinity of C is reached, and C is not a peak, but a protuberance. The curve becomes practically straight again after C. The point B ceases to be a peak if q_1 is rather less than 5, and begins to resemble C.

Perhaps the main points of interest about the curve are, next to its approximation to that for H_α, the straightness of its branches and the smallness of the protuberances. But, in spite of their smallness, the method already described of using paper printed in a pattern of fine dots enables them to be detected readily by pricking out the final dot which is visible on the enlarged photograph. The distance between the protuberances on either side of the axis, divided by the magnification, gives at once twice the separation of the components from the central line on the original plate, and allows at the same time for the fact that the prismatic spectrum is not normal.

It is to be noted that the ratios of the slopes of the nearly straight branches of the curve differ little from those of the values of q belonging to the components, when these values decrease so rapidly that the peaks become mere protuberances.

Since the head of a protuberance on the curve lies necessarily on the axis of the component giving rise to it, the particular constant intensity which defines the contour is immaterial. If, therefore, a set of contours of various constant intensities are chosen on the plate, the heads of the various protuberances, one on each contour, due to any component, lie on a straight line parallel to the axis of the contours, or perpendicular to the base of the photograph. Protuberances of very small size can in this way be detected as such, without the risk of including slight irregularities in the contour which might be due to defects in the grain of the plate, and at the same time, the axes of the components can be defined with some degree of precision.

We now come to the precise values of the separations determined from the photographs of H_α. The contour exhibits three definite protuberances on each side at the same heights, and satisfying the conditions just specified. On one of the photographs of magnification 20·3 the breadths between the protuberances are 10·8, 23·0, and 35·5 mm., respectively. These are in the ratios 1 : 2·13 : 3·29. The separation of the three closest components in STARK's experiments* are 2·6, 6·2, and 8·8 Å.U., which are in the ratios 1 : 2·38 : 3·29. The agreement is striking. Moreover the separation of the next component in STARK's experiments is 11·5 Å.U., from which we deduce that the breadth at the next protuberance should be 47·7 mm. But the whole breadth of the base of the photograph is about 39 mm., and therefore with the degree of exposure given this component could not appear. The existence, therefore, of components whose separations are in the same ratio as those found by STARK appears to be established, and affords a strong confirmation of the view that the main factor which controls the broadening is the electrical resolution of the lines. The corresponding phenomena for H_β are much more complicated, and the determination of the attenuation-ratios and intensities of the components may, therefore, be deferred for subsequent treatment.

(X.) *The Diffuse Series of Helium and Lithium.*

The intensity distribution in broadened lines in the spectrum of helium has been investigated in the same manner as in the case of hydrogen, but the quantitative intensity distribution has not yet been determined. The spectrum was produced by passing condensed discharges through a vacuum tube containing helium with a spark-gap in the circuit. The results are qualitatively in accordance with the intensity distribution to be expected from the electrical resolution of the lines. The broadening of the line $\lambda = 4471$ is particularly striking, and it appears to consist of a bright component of great intensity and a broader displaced component. STARK* has found that the electrical resolution of this line is unsymmetrical and that the intensity of the central components is very small. Since it has been shown that the breadth of a component increases with its distance from the unresolved line, we should expect the above distribution of intensity in the line $\lambda = 4471$. On the other hand, the line $\lambda = 4026$ appears to consist of a bright central component with nebulous "wings," which is also in agreement with theory.

It may be mentioned that by the use of the wedge method the relative differences in the intensities of the lines which occur when a condensed discharge or an uncondensed discharge is employed can at once be seen. In the case of helium this is particularly interesting. With the condensed discharge the two diffuse series are relatively much more intense than with the uncondensed discharge. It is remarkable also that by far the greatest increase in relative intensity is found to occur in the line $\lambda = 4471$, whilst the D_3 line, the preceding member of the series, is affected to a smaller degree. This result, whilst affording no explanation, indicates the possibility

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* *Loc. cit.*

of reproducing in the laboratory the intensity relations which are found in the spectra of certain stars, in some of which the line $\lambda = 4471$ is the most intense of the helium lines seen, whilst under ordinary conditions of excitation by uncondensed discharges at moderate pressures the D_3 line is the strongest line in the spectrum, and at low pressures the line $\lambda = 5015$ becomes the most conspicuous.

An investigation of the lines of the diffuse series of lithium with the use of the neutral wedge has not yet been made, but qualitative results for these lines, photographed with the concave grating spectrograph, confirm the view that the Stark effect is mainly responsible for the phenomena observed. It is, of course, impossible to control the experimental conditions when spectra are produced in the electric arc, and the results may be complicated by reversal. The peculiar character of these lines has been noted by numerous investigators. More especially the complex appearance of the line $\lambda = 4602$ has been investigated by HAGENBACH[*] and by RAMAGE.[†] If the vapour is dense, reversal may be observed in the line $\lambda = 6103$. For less dense vapours the line $\lambda = 6103$ is not reversed nor the line $\lambda = 4132$, but the line $\lambda = 4602$, which belongs to the same series and lies between these lines, gives the impression of an extremely unsymmetrical reversal. These appearances of the three lines have been recorded photographically on the same plate, using as a source of light a carbon arc containing a suitable quantity of lithium. It would appear extremely improbable that the apparent reversal of the line $\lambda = 4602$ is real, since the lines preceding it and following it in the series do not show the phenomenon. This result, however, is precisely what we should predict on the supposition that the appearance of the lines depends mainly on the Stark effect.

According to STARK (*loc. cit.*) the electrical resolution of $\lambda = 6103$ consists of a small displacement, but this result is probably incomplete. For the line $\lambda = 4602$ the central undisplaced components, when the line is resolved, are either very weak or absent, and the displaced components are unsymmetrically arranged with respect to the unresolved line in the same direction as the asymmetry of the line as seen in the arc. In the case of the line $\lambda = 4132$ there are components of considerable intensity very slightly displaced from the unresolved line. A minimum unsymmetrically localised in the broadened line is therefore precisely what we should expect for the line $\lambda = 4602$, a phenomenon which we should not expect, and do not find, in the lines $\lambda = 6103$ and $\lambda = 4132$. In cases such as this, it is not improbable that the broadening of the lines may be affected by the potential fall between the poles of the arc, and indeed such phenomena as the "pole effect," or the small changes of wave-length which have been found to occur in the neighbourhood of the poles of the arc, may ultimately be explained in this way. In this case any contribution to the phenomenon of the direct action of the potential fall between the poles might be detected by polarizing the light. It may also be necessary to consider whether many

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[*] 'Ann. d. Phys.,' (4), 9, p. 729, 1902.

[†] RAMAGE, 'Roy. Soc. Proc.,' vol. 71, p. 164, 1903.

apparent cases of reversal are not in fact spurious, having no relation to true reversal, due to absorption.

Finally, the different character of lines of the same series in the spectra of the alkaline earth metals which has been noted by ROYDS[*] may be expected to fall into line with their electrical resolution when the necessary data are available.

(XI.) *Ultraspectroscopic Analysis by Means of the Neutral Wedge.*

It may be mentioned that the neutral wedge as an accessory to the spectroscope virtually increases its resolving power. The intensity distribution of the image of an infinitely narrow line, as seen in a spectroscope of known resolving power, is precisely defined, and analysis by means of the neutral wedge enables us to build up a system, both as regards position and intensity, which conforms with the curve experimentally found. It is therefore evident that with this accessory the practical resolving power of the spectroscope depends only on its dispersion, and is independent of the theoretical purity of the spectrum. In conjunction with the interferometer it may be expected to give results beyond the attainment of pure spectroscopic analysis.

It may reasonably be hoped that the application of such methods may enlarge our knowledge of the structure of the finest spectrum lines.

(XII.) *Summary.*

(1) A method has been described, involving the use of a neutral-tinted wedge, by means of which the actual distribution of intensity in broadened spectrum lines can be accurately measured.

(2) With this arrangement quantitative measurements of the hydrogen line H_α have been made, and qualitative observations of other lines of hydrogen, helium, and lithium.

(3) The intensity distribution of lines, broadened by condensed discharges and at high pressures, does not follow the well-known probability law, which is known to obtain under certain specified conditions.

(4) The broadening of H_α is symmetrical.

(5) The most general characteristic of all the curves obtained is that their curvature is away from the axis perpendicular to the wave-length scale. It is shown that even in the case of a simple curve, such as that found for H_α, this is inconsistent with the view that a single component is involved.

(6) The existence of more than one component is in accordance with the view that the electrical resolution of the lines is the origin of their broadening.

(7) On the supposition of several components, symmetrically distributed about the

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[*] *Loc. cit.*

centre, the only general law consistent with the distribution of curvature is that of a sum of linear exponential terms, one for each component.

(8) It is shown that under these circumstances discontinuities in the slope of the curves must occur. The discontinuities which have been found in the curve for H_α are in quantitative accordance with those to be expected from the available data with respect to the electrical resolution.

(9) Qualitative observation of H_β, H_γ and the diffuse series of helium and lithium confirms the view that electrical resolution is the principal cause of the phenomena.

(10) A discussion of further applications of the method is given.

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